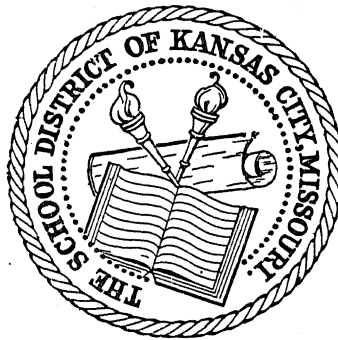


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TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Volume 143

INSTITUTE OF METALS DIVISION
1941

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT MEETINGS HELD AT
CLEVELAND, OCTOBER 21-23, 1940, AND NEW YORK FEBRUARY 17-20, 1941

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Notice

This volume is the fifteenth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the Cleveland Meeting, Oct. 21-23, 1940, and the New York Meeting, Feb. 17-20, 1941. The complete list of publications and proceedings, including the present volume, is as follows:

1908-1911 *Transactions* of the American Brass Founders' Association: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.

1912-1916 *Transactions* of the American Institute of Metals, Vols. 6-10.

1917-1918 *Journal* of the American Institute of Metals, Vols. 11-12.

1919-1926 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.

1927-1928 PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the later is now designated Vol. 78 of the A. I. M. E. TRANSACTIONS.

1929-1941 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 83, 89, 93, 99, 104, 111, 117, 122, 124, 128, 133, 137 and 143, Institute of Metals Division.

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Reference

FOREWORD

DURING the fifteen years in which there has been a separate Institute of Metals Division volume of the TRANSACTIONS, there have thus been published just short of 400 technical papers comprising upward of 7000 pages. The present volume, containing 29 papers, is one of the largest of this series. However, quality has not been sacrificed for mere size, and the officers of the Division are proud of the caliber and scope of the papers here published.

The annual lecture this year was given by Professor George Sachs, generally acknowledged as one of the world's outstanding physical metallurgists and one who contributed much to the literature of nonferrous metals. This lecture, on "Some Fundamentals of the Flow and Rupture of Metals," is an outstanding one, being somewhat unusual in that it held a strong appeal both to the theoretical and practical metallurgist.

Possibly the membership at large does not realize how much the success of the programs and therefore of this volume depends on the Papers and Programs Committee, and this opportunity is taken to thank Dr. Cyril S. Smith, Chairman, Mr. E. E. Schumacher, Vice Chairman, and the other members of that committee for the excellent work done.

As Chairman of the Division, I also extend my sincere thanks to the other officers of the Division and Chairmen of the various committees, who have all cooperated toward a successful Division year.

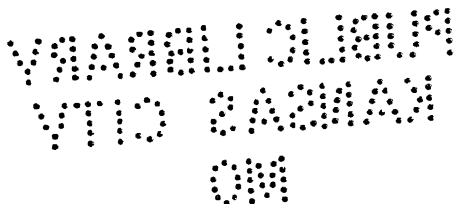
Thanks are also due the personnel of the Institute office, without whose help the Chairman would find himself most seriously handicapped. In this connection, it is felt that all of the members will regret to know that Mr. Louis Jordan, who for several years did so fine a job as Secretary of the Division, left in March to take a position with the O.P.M., in Washington, where no doubt his talents will be used to good advantage. The Division is fortunate, however, in obtaining the services of Mr. Frank T. Sisco to fill the office vacated by Mr. Jordan.

D. K. CRAMPTON, *Chairman*,
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Established as a Division April 26, 1918

(Bylaws published in the 1939 TRANSACTIONS Volume of the Division.)

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ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF METALS DIVISION

In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February. There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

- 1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmānstätten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. *TRANSACTIONS* (1931) **93**, 78–110.
- 1935 E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. *TRANSACTIONS* (1934) **111**, 264–292.
- 1936 Cyril S. Smith and W. Earl Lindlie: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. *TRANSACTIONS* (1933) **104**, 69–105.
- 1937 Arthur Phillips and R. M. Brick: Effect of Quenching Strains on Lattice Parameter and Hardness Values of High-purity Aluminum-copper Alloys. *TRANSACTIONS* (1934) **111**, 94–112.
- 1938 William L. Fink and Dana W. Smith: Age-hardening of Aluminum Alloys, I—Aluminum-copper Alloy. *TRANSACTIONS* (1936) **122**, 284–293.
- 1939 Frederick N. Rhines and Robert F. Mehl: Rates of Diffusion in the Alpha Solid Solutions of Copper. *TRANSACTIONS* (1938) **128**, 185–221.
- 1940 Alden B. Greninger: Martensite Transformation in Beta Copper-aluminum Alloys. *TRANSACTIONS* (1939) **133**, 204–221.
- 1941 S. E. Maddigan and A. I. Blank: Recovery and Recrystallization in Long-time Annealing of 70-30 Brass. *TRANSACTIONS* (1940) **137**, 170–190.

THE INSTITUTE OF METALS LECTURE

An annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

- 1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
- 1923 Solid Solution. By Walter Rosenhain.
- 1924 The Trend in the Science of Metals. By Zay Jeffries.
- 1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
- 1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
- 1927 Growth of Metallic Crystals. By Cecil H. Desch.
- 1928 Twinning in Metals. By C. H. Mathewson.
- 1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
- 1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
- 1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
- 1932 The Age-hardening of Metals. By Paul D. Merica.
- 1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.
- 1934 Ferromagnetism in Metallic Crystals. By L. W. McKeehan.
- 1935 Gases in Metals. By C. A. Edwards.
- 1936 Diffusion in Solid Metals. By Robert F. Mehl.
- 1937 Refractories. By R. S. Hutton.
- 1938 The Nature of Metals as Shown by Their Properties under Pressure. By P. W. Bridgman.
- 1939 The Creep of Metals. By D. Hanson.
- 1940 Acceleration of Rate of Corrosion by High Constant Stresses. By Edgar H. Dix, Jr.
- 1941 Some Fundamentals of the Flow and Rupture of Metals. By George Sachs.



GEORGE SACHS

Institute of Metals Division Lecturer, 1941

Some Fundamentals of the Flow and Rupture of Metals

BY GEORGE SACHS,* MEMBER A.I.M.E.

(Institute of Metals Division Lecture†)

I deeply appreciate the honor of being selected to deliver the twentieth Annual Lecture of the Institute of Metals Division.

The subject of my paper is extremely involved and voluminous, therefore I shall discuss only some more recent experimental material and speculate somewhat on the physical and mechanical fundamentals of these changes.

The flow and the rupture of a solid material are rather different phenomena. It is therefore surprising that up to a rather advanced stage in metallurgical science these two fundamental phenomena have been simultaneously treated and forced into the general conception of the "failure" of solid material. Only in this century, and particularly during the last 20 years, have the very different physical meanings of flow and rupture been clearly recognized. Several hundred of the more recent publications deal with these subjects.¹

LAW OF SIMILARITY

The basic values commonly considered responsible for the mechanical behavior of any material are the stresses. From this standpoint both a large and a small article made from the same homogeneous metal and of geometrically similar shapes should behave identically, i.e., they should deform geometrically in a similar manner, if subjected to the same stress values at corresponding points. This "law of similarity" was introduced about 60 years ago simul-

aneously by Barba² and Kick³ and was derived from the classical theory of elasticity.

As far as the plastic behavior of a metal is concerned, this rule appears to be valid. The conventional properties of large and small tension or compression test bars, machined from larger sections, are identical; while the force required to deform a section is proportional to its cross-sectional area and the work consumed in deforming geometrically similar articles in a geometrically similar manner is proportional to its volume. The general trend of the stress-strain diagram of a metal is independent of the section size (Fig. 1). No exceptions from this rule are known.

However, if the deformation of a metal is continued until rupture occurs, and the breaking stress or the work consumed is measured, a test bar of large cross section appears to fail before or at lower stresses than does one having a small cross section. Thus, the specific impact energy has been often found to decrease with increasing size of the test specimen, particularly for materials with a limited ductility.⁴ Another exception from the rule of similarity is offered by fatigue-strength values, which usually decrease with increasing section size.^{5,6}

The conclusion must be drawn from these experimental facts that the ductility of a homogeneous metal decreases with increasing section size (Fig. 1). This effect has been actually confirmed by Docherty,⁷ who observed that in static notch bending tests large specimens failed earlier and in a more brittle fashion than small specimens ma-

* Associate Professor, Metallurgical Department, Case School of Applied Science, Cleveland, Ohio.

† Presented at the New York Meeting, February 1941. Twentieth Annual Lecture. Manuscript received at the office of the Institute Jan. 24, 1941. Issued as T.P. 1335 in METALS TECHNOLOGY, June 1941.

¹ References are at the end of the paper.

chined from the same section (Fig. 2). It also appears to be common commercial experience that small sections can be cold-reduced much further than large sections.

It may be mentioned in this connection that none of the conventional mechanical

tests has been continuously in the investigation of various commercial forming tests.^{9,10,11}

THEORIES OF PLASTICITY

The next problem regarding the flow and rupture of a metal is that of the effect of

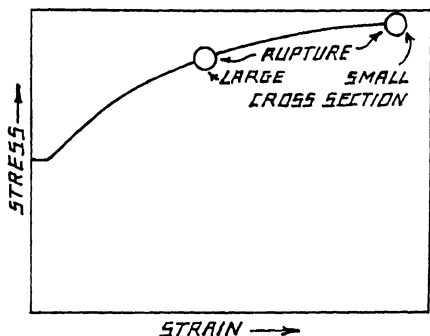


FIG. 1.—DIAGRAMMATIC REPRESENTATION OF STRESS-STRAIN DIAGRAM FOR A LARGE AND A SMALL CROSS SECTION.

tests give any measure for the ductility corresponding to the behavior of the metal in working or in service. Certainly, the elongation in a tensile test has little relation to the actual ductility; and the contraction in area at the rupture of a tensile test may indicate losses of ductility in some cases, but completely fails to do so in others. For example, the very ductile annealed duralumin has about the same contraction in area as the much brittler heat-treated condition. Also, a steel heat-treated to a high hardness frequently shows a higher contraction in area than it does in a softer condition, which is contrary to that indicated under actual performance. It is also known that small inclusions, such as the oxides in steel and copper,⁸ considerably reduce the contraction in area in tension tests, but have comparatively little effect on the general ductility. Other tests, such as the various bending or forming tests, have not been sufficiently explored with respect to ductility. In fact, little has been done up to the present time to analyze this fundamental property, while a large amount of work is being expended con-

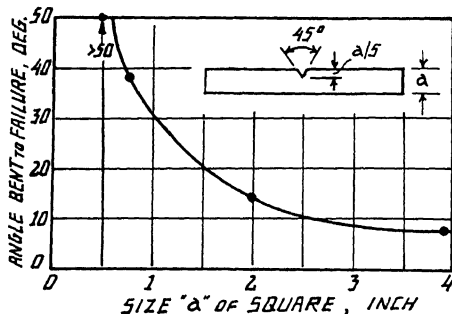


FIG. 2.—EFFECT OF SECTION SIZE ON DUCTILITY OF NOTCHED MILD STEEL BARS SUBJECTED TO BENDING (DOCHERTY).

various types of stresses, such as tension, compression and shear, and of combinations of these simple types of stresses.

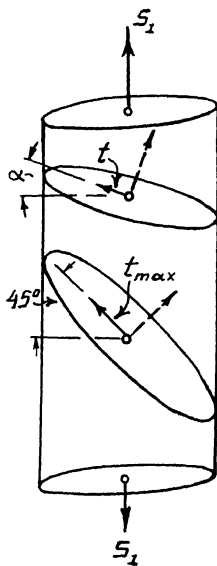


FIG. 3.—DIAGRAMMATIC REPRESENTATION OF SHEAR STRESSES ACTING ON DIFFERENT PLANES OF STRESSED ROD.

As far as the flow of the metal is concerned, it was found in an early stage of

scientific metallurgy¹ that the principal determining factor is the maximum value of the shear stresses that are created in a strained metal (Fig. 3). If a metal is sub-

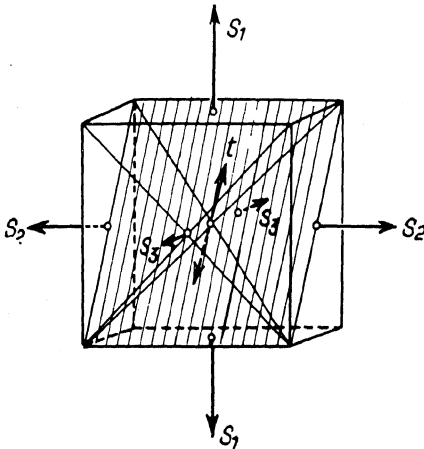


FIG. 4.—RELATION OF MAXIMUM SHEAR STRESS TO PRINCIPAL STRESSES.

jected to any combination of homogeneous stresses, shear stresses are created in any section, on any imaginary set of planes. In one particular plane this shear stress, t_{\max} will be larger than in any other plane. According to the "maximum shear stress" hypothesis, a metal will flow under any combination of stresses (or "stress state") if the maximum shear stress reaches a critical value.

While this conception at first appears very lucid and reasonable, a simple conclusion reveals that it is incompatible with the facts. According to general experience, a strained metal can progressively assume any desired cross-sectional shape; the dimensions can increase or decrease, depending upon the particular combination of applied stresses and determined by the shape of the tools. However, in a strained metal one and only one set of planes will usually exist where the shear stress is higher than that on any other set (Fig. 4). This set is, according to the laws of elasticity, the set of planes that are inclined at an angle of 45° to both the directions of the

largest and the smallest normal or principal stress (designated s_1 and s_3 , respectively). The maximum shear-stress law postulates that this shear stress determines the plastic

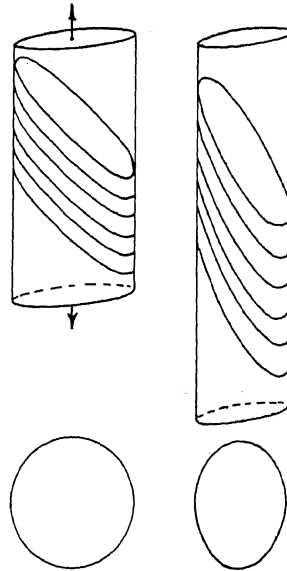


FIG. 5.—DIAGRAMMATIC REPRESENTATION OF CHANGE OF GENERAL SHAPE OF ROD IN WHICH ONLY ONE SYSTEM OF SLIP PLANES ACTS.

flow, which therefore will occur only in the direction of the shear stress. This, however, creates a rather restricted and special type of deformation (Fig. 5). A round section will be converted into an elliptical one, without any change of the one transverse dimension. And the change of shape will not be affected by any stress acting in this transverse direction, as long as this stress does not become predominant.

An alternative conception was introduced as early as 1870 by the French scientists St. Venant¹² and Lévy,¹³ who compared the flow of solid metals to that of liquids. A liquid will flow in all directions, the extent of these strains depending upon the ratios of the corresponding stresses and changing continuously with the stresses. Such a continuous relation between stresses and strains (Fig. 6) has been confirmed in recent investigations.¹⁴ Any modern theory

of plasticity must be based on the assumption of such a continuous relation.

While mathematicians have proposed numerous more or less complicated combi-

tubing, which is simultaneously subjected to a controlled internal pressure (Fig. 7).

The other experimental fact, which will be discussed later in a more detailed

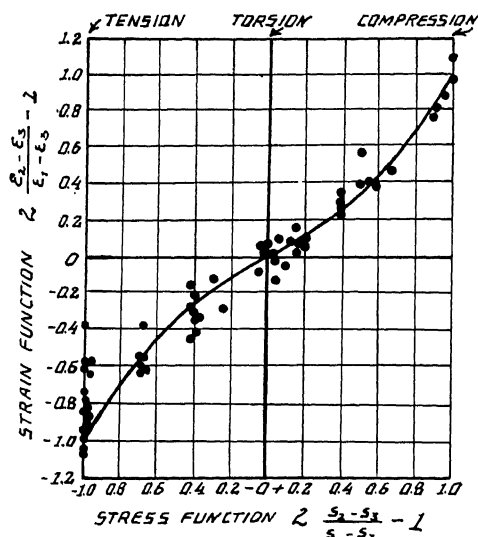


FIG. 6.—RELATION BETWEEN STRESSES AND STRAINS IN PLASTIC FLOW OF SOME METALS (LODE).

nations of stresses as the fundamental factor responsible for the flow of metals, extensive experimental work has revealed two important facts.^{14,15}

First, it has been found that when varying the stresses in any possible manner the maximum shear stress during flow will vary with the stress combination, but only between the yield strength in tension or compression and a value approximately 10 to 15 per cent higher than the yield strength (Fig. 7). This highest value of flow resistance will be observed in any strain condition where one dimension is not changed, as in rolling. This strain state also occurs in torsion.

Another stress state of this type, which can be experimentally investigated in an exact manner, is realized in a tube that is being subjected to tension in two directions, longitudinally and circumferentially, the one tension being twice as high as the other ($s_1 = 2s_2$). The experimental procedure consists of tension tests on thin-walled

manner, is that the addition of hydrostatic pressure affects only slightly the flow stress. This variation can be neglected as far as the stresses encountered under commercial conditions are concerned.

The theory that quantitatively agrees with the experimental facts is the so-called "strain-energy theory" advanced by v. Mises¹⁶ and Haigh.¹⁷ This conception considers the totality of the shear stresses or the sum of the squares of the shear stresses responsible for the plastic flow, according to the following formula:

$$4(t_1^2 + t_2^2 + t_3^2) = (s_2 - s_3)^2 + (s_3 - s_1)^2 + (s_1 - s_2)^2 = 2s_n^2$$

where t_1, t_2, t_3 indicate the three principal shear stresses, s_1, s_2, s_3 the three principal normal stresses and s_n the yield strength in tension (or compression). This theory has attracted considerable attention and appears to represent the closest approach to experience that can be treated mathematically in a fairly simple manner. Fre-

quently, however, the simpler maximum shear-stress theory will be sufficiently accurate for practical purposes.

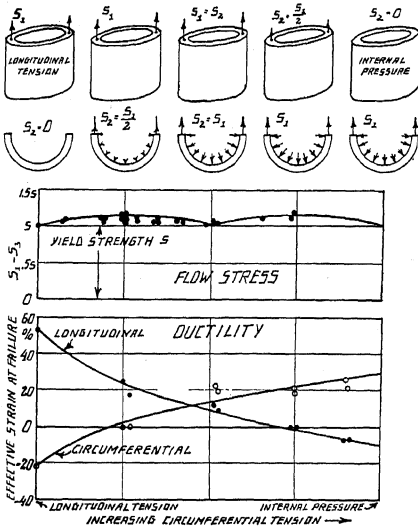


FIG. 7.—EFFECT OF BIAxIAL TENSION ON FLOW STRESS AND DUCTILITY OF STEEL TUBES.

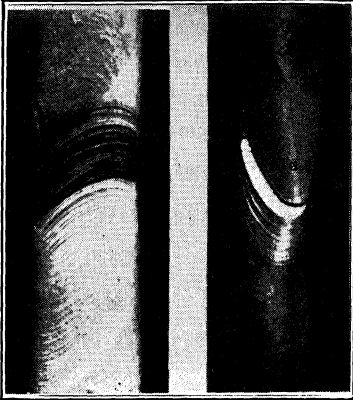


FIG. 8.—SINGLE BRASS CRYSTAL, STRETCHED IN TENSION TO BREAKING POINT.

On the other hand, no lucid physical conception is associated with the shear-strain theory. Attempts have been made, therefore, by Sachs¹⁷ and, more completely, by Cox and Sopwith¹⁸ to develop a condition of plasticity from the fundamental conceptions of plastic flow of single crystals. Single crystals usually are rod or plate-shaped samples consisting of only

one crystal grain (Fig. 8). Such a single crystal flows if the shear component (Fig. 9) on a crystallographic plane, the slip

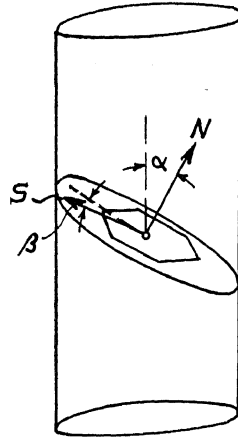


FIG. 9.—DIAGRAMMATIC REPRESENTATION OF SLIP SYSTEM OF SINGLE CRYSTAL. N , normal to slip plane. S , slip direction.

plane, in a crystallographic direction, the slip direction, reaches a critical value. The principal stresses required to produce plastic flow in a single crystal therefore

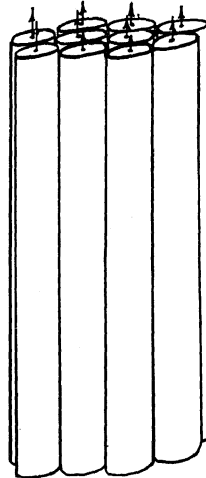


FIG. 10.—DIAGRAMMATIC REPRESENTATION OF GROUP OF SINGLE CRYSTALS STRAINED IN TENSION.

depend upon the angles between the slip-plane direction and the directions of stress, these yield-strength values usually varying

considerably for differently oriented crystals (Fig. 15). The total average of this flow stress for a group of crystals, consisting of all possible orientations (Fig. 10),

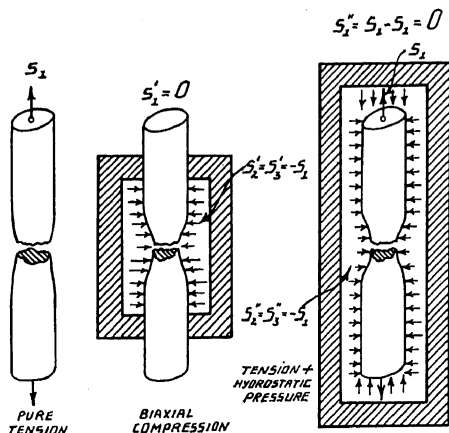


FIG. 11.—DIAGRAMMATIC REPRESENTATION OF FRACTURES CAUSED BY VARIOUS STRESS STATES.

can be numerically calculated for various stress states. It has been found that the average maximum shear stress will differ by about 15 per cent for the two extreme conditions of pure tension and of biaxial tension with the one tension twice the value of the other. These rather tedious calculations show that fundamentally the flow of a homogeneous crystalline aggregate is determined by crystallographic phenomena. Unfortunately, however, the crystallographic theory of plastic flow has not been sufficiently advanced to be expressed by simple equations, which can be readily used for calculations.

There exists one rather unsatisfactory exception to the laws that determine the beginning of plastic flow. This is annealed low-carbon steel, which usually flows when the maximum shear stress reaches a constant value, not dependent upon the other components of the stress state.¹⁴ This relation also appears to be associated with the presence of the familiar yield-point elongation or jog in the stress-strain diagram. At the present time, these phenomena have

not been adequately explained. While the conception of a brittle grain-boundary skeleton in the soft steel²⁰ explains some of the features of the yield point, it does not permit any positive conclusion regarding the conditions required for the beginning of plastic flow.

Apparently there is another fundamental conception that does not apply to soft steel. As previously discussed, it is usually assumed that a metal will flow locally if the stresses in a small volume correspond to the plasticity conditions. No deviations from this law have been observed for most metals. Soft steel, however, according to some accurate measurements²¹ will withstand in localized areas, such as around a hole in a stressed beam, stresses more than 2.5 times the expected values without plastic flow. Apparently soft steel behaves differently under uniform than under non-uniform stress conditions where high stress gradients exist.

EFFECT OF HYDROSTATIC PRESSURES ON PLASTIC FLOW

Large variations in the stress state can be realized by carrying out experiments in a high-pressure chamber. This has been done particularly by Bridgman²¹ and numerous unusual changes of physical properties have been found to occur with increasing pressures. These pressures are of the hydrostatic type or of the same magnitude in all directions.

The resistance to plastic flow is also somewhat increased by the addition of hydrostatic pressure. The rate of increase with increasing pressure, however, is comparatively small and can be neglected as far as the commercial behavior of the metals is concerned, as previously mentioned. This is expressed by the relation that the maximum shear stresses are not affected by the addition or subtraction of a hydrostatic pressure ($-p$):

$$\tau_{\max} = (s_1 - p) - (s_3 - p) = s_1 - s_3$$

It has been observed also that hydrostatic pressures do not affect the strain conditions or type of plastic flow in metals. This may result in somewhat unusual

fractures. Thus, biaxial pressure results in a tension-type failure, while, correspondingly, biaxial tension produces a compression-type strain.

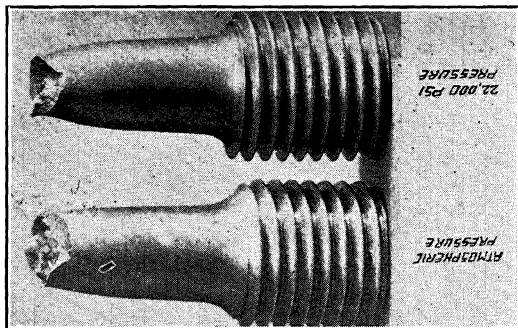


FIG. 12.—FRACTURES OF CAST STEEL SUBJECTED TO PURE TENSION AND TO BIAxIAL COMPRESSION (ROS AND EICHINGER).

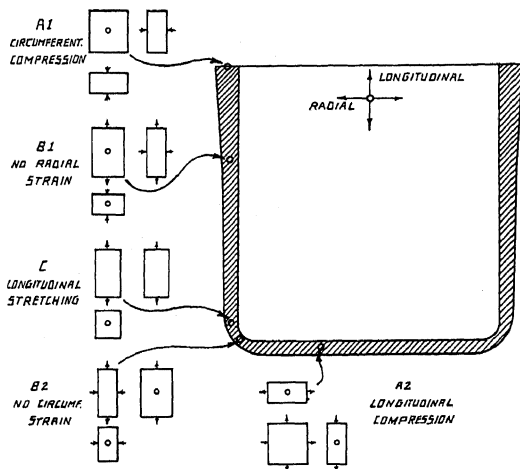


FIG. 13.—DIAGRAMMATIC REPRESENTATION OF VARYING STRAIN CONDITIONS IN A DEEP-DRAWN SHELL.

Small arrows indicate stresses acting at respective points.

phenomena, as reported by Bridgman.²² If a cylindrical bar is passed through a container and subjected to a high biaxial pressure ($s'_2 = s'_3$) this bar fails (Fig. 11) in fundamentally the same manner as a regular tension test bar (Fig. 12), disregarding the fact that only compression stresses are present. This is explained by the mechanical relation that biaxial pressure is identical with tension plus a superimposed hydrostatic pressure of the same magnitude as the tension stress (Fig.

Generally, the same strain condition can be created by an infinite number of stress states, which, however, differ only by the hydrostatic pressure applied.

This is confirmed also by the observation that the alignment of the crystal grains in a specific metal depends only upon the general change of shape or strain conditions.^{24,25} Thus various processes, such as tension, drawing, rolling or swaging a rod to the same final shape result in the same fiber structure. A particularly instructive

illustration is offered by a drawn cup in which, according to Herrmann and Sachs,²⁵ virtually all possible strain conditions are realized (Fig. 13). The compression-type strain A occurs at the edge of the cup, which is subjected mainly to circumferential compression A_1 , and also in the bottom A_2 where biaxial tension acts. A condition similar to rolling, in which one dimension is not changed (B) is also found at two points, somewhere in the upper part of the wall (B_1) where the original thickness of the blank is preserved and at the corners (B_2) where the fibers are mainly stretched but the diameter of the blank is retained. Near the latter point, a tension-type strain and stress (C) occur. The X-ray analysis of the different points has revealed only one series of fiber structures, these being determined by the respective strain conditions and not by the widely varying stress conditions.

EFFECT OF STRESS STATE ON DUCTILITY

The rupture of a metal, on the contrary, is decidedly affected by the stress state, and particularly by the superposition of hydrostatic stresses.

While a general theory of the rupture of metals has not yet been developed, it is apparent that the majority of service failures can be attributed to the presence of excessive tension stresses.²⁶

Therefore, the superposition of a hydrostatic pressure, which reduces the tension, also diminishes the tendency to rupture and increases the ductility. This has been particularly observed with rocks that usually are brittle but become increasingly plastic with increasing hydrostatic pressures.^{27,28}

This effect is less pronounced with metals which are, in most cases, fairly ductile in ordinary atmospheric pressures. However, the ductility of any metal is also considerably increased by the addition of hydrostatic pressures,¹⁴ as illustrated in Fig. 12 for the contraction in area of a cast

steel, and in Fig. 14 for the stress-strain diagrams of an aluminum bronze in tension and cast iron in compression.

The beneficial effect of hydrostatic pressures is being widely utilized in the manufacture and fabrication of the metals. There are two basic methods of creating high pressures. The first is the use of closed passes or dies, as in die forging, rod rolling or extruding, which force the metal to flow through narrow orifices. The second is the presence of high friction forces, which will be discussed later in detail. The objective is to eliminate tension stresses in order to reduce the tendency for brittle fractures.²⁶

Another aspect of this problem is equally important. Any superimposition of hydrostatic tension should increase the tendency to rupture and consequently reduce the ductility. In the extreme case of high triaxial tension, any material should behave in a completely brittle manner. While such a condition may be approached in practice, as in quenching or welding, it can be experimentally realized and followed up only to a very limited extent. The most lucid experimental evidence of an embrittling effect of multiaxial tension has been again observed in tubing that is simultaneously subjected to longitudinal and circumferential tension.^{29,30} By increasing the latter to a value where it becomes 50 per cent of the longitudinal tension, the ductility, measured by the local contraction or elongation at the failure is reduced materially (Fig. 7). Thus an additional transverse tension has a pronounced embrittling effect.

The presence of such transverse tension also accounts for the much discussed effects of sharp notches on the tensile properties of the metals.^{31,32,33} Practical experience evidently indicates that external or internal notches are a frequent and important source of service failures of the brittle type. However, the results so far published on this subject disagree with the theoretical

conceptions³⁴ therefore a discussion of this subject must be postponed until new experimental data are available.

by Schmid³⁶ and the amount of movement in this direction or shear strain, suggested by Sachs.³⁷ With these units, the stress-

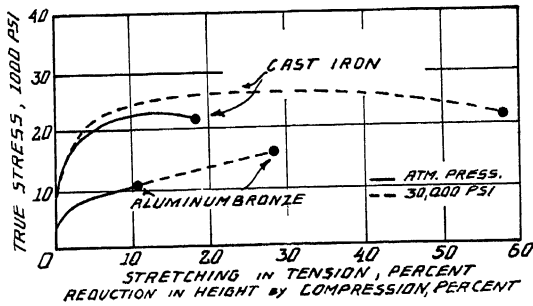


FIG. 14.—EFFECT OF HYDROSTATIC PRESSURE ON DUCTILITY OF CAST IRON (COMPRESSION) AND ALUMINUM BRONZE (TENSION) (ROS AND EICHINGER).

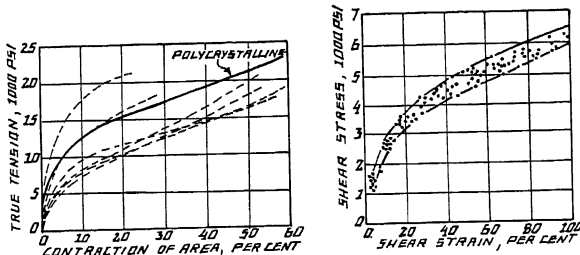


FIG. 15.—STRESS-STRAIN DIAGRAMS OF SINGLE ALUMINUM CRYSTALS IN DIFFERENT ORIENTATIONS AND USING MECHANICAL AND CRYSTALLOGRAPHIC COORDINATES, RESPECTIVELY.

STRESS AND STRAIN OF SINGLE CRYSTALS AND OF POLYCRYSTALLINE AGGREGATES

Plasticity is a basic property of metallic crystals. During the last 20 years the mechanical properties of single crystals have been studied extensively^{35,36} and it has been found that differently oriented single crystals of a specific metal usually show widely varying stress-strain diagrams for any type of testing, such as tension, compression or torsion (Fig. 15). These diagrams can be converted into a single characteristic curve by replacing the conventional mechanical stress and strain units, such as tension and reduction in area (or elongation) by corresponding crystallographic units. These crystallographic units are the shear-stress component on the slip plane in the direction of slip, proposed by Taylor and Elam³⁵ and

strain diagrams for differently oriented crystals of aluminum³⁸ and zinc³⁶ are almost identical (Fig. 15), and the same stress-strain curve is obtained in tension and in compression.³⁹

The yield strength, the strain-hardening and correspondingly the ultimate strength of a ductile polycrystalline aggregate is always considerably higher than the average strength of the single crystals that constitute the aggregate (Fig. 15). To explain this difference, many metallurgists have accepted Beilby's hypothesis of very hard and strong amorphous layers in the grain boundaries of the individual crystal grains. However, any attempt to prove the existence of such amorphous metal has been unsuccessful.

On the contrary, Chalmers⁴⁰ found that the presence of a longitudinal grain boundary in "bicrystal" tin specimens increases

the yield strength only, if the two crystal grains differ in their orientation, and that the increase is approximately proportional to this difference in orientation (Fig. 16).

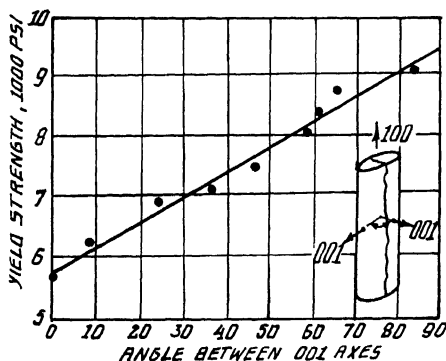


FIG. 16.—YIELD STRENGTH OF TIN SPECIMENS CONSISTING OF TWO CRYSTALS WITH LONGITUDINAL BOUNDARY (CHALMERS).

Thus, the difference in strength between single crystals and a polycrystalline aggregate can be explained by the fact that adjacent crystals mutually obstruct their crystallographic deformation. While a single crystal becomes oval in tension (Fig. 8), the crystal grains in an aggregate are being forced to alter their shape to correspond to the general change of shape of the strained article. According to Taylor⁴¹ this results in complex slip movements within the crystals accompanied by an increased strain-hardening. If differently oriented crystals are forced into a given shape, five different gliding systems become active. The extent of the shear movement occurring on each gliding system and the sum of these shears on various gliding systems can be calculated, and the corresponding strain-hardening can be determined from the stress-strain diagram of a single crystal. The stress-strain diagram of a polycrystalline aluminum calculated on this basis agrees with the experimentally observed curve (Fig. 17). So far, this tedious calculation has been carried out only for tension.

This superposition of various slip movements also explains the preferred orienta-

tion that occurs on cold-working. In a single crystal, any strain will cause the crystal lattice to rotate in such a manner that some important crystal directions approach the directions of strain. Fundamentally, the same reorientation process takes place in the grains of a polycrystalline metal. This "fibering," however, is more complicated than and different from that of single crystals. According to Taylor,⁴¹ the changes in orientation of the individual crystal grains can be calculated from the slip movements required to alter the external shape during deformation. While this theory offers an approach to the solution of the extremely complex problem of crystallographic fibering during working, investigations by Barrett⁴² indicate that it needs further refinement in order to satisfactorily explain the experimental evidence.

The crystallographic fibering also determines to a certain extent the physical and mechanical properties in worked and in annealed metals (Fig. 18). Some metal products are commercially produced with such a pronounced preferred orientation that their structures and properties approach those of a single crystal. Thus, in annealed copper sheet, all crystal grains may be, within certain limits, aligned with the axes of their cubic crystal lattice parallel to the rolling, transverse and normal directions,^{36,43,44} and such sheet with a "cubic structure" has directional properties almost corresponding to those of a single crystal (Fig. 18); i.e., specimens taken in different directions have very different properties. The agreement between the properties of such sheet and those of a similarly oriented single crystal is particularly good with respect to the elastic properties.⁴⁴ The same is true for the magnetic qualities of iron-nickel alloy sheet⁴⁵ and iron-silicon alloy sheet, the latter being commercially produced with a highly preferred orientation and directionality of the magnetic properties.^{46,47}

While considerable progress has been made during recent years regarding the fundamental conceptions of the plastic flow in single crystals and polycrystalline

not apply when plastic flow precedes the failure; and this deformation introduces complicated and as yet not explained phenomena. Single crystals of the more

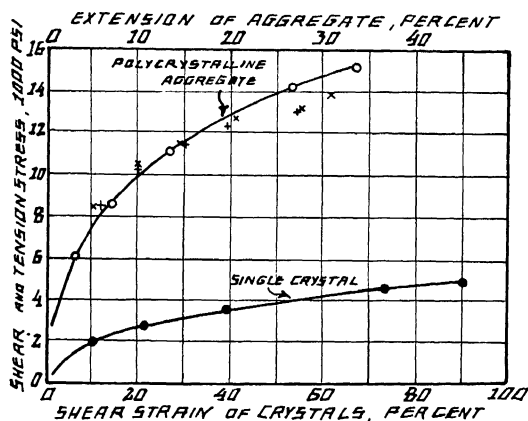


FIG. 17.—TENSION-EXTENSION CURVE OF POLYCRYSTALLINE ALUMINUM, DERIVED FROM SHEAR STRESS-SHEAR CURVE OF SINGLE CRYSTAL (TAYLOR).

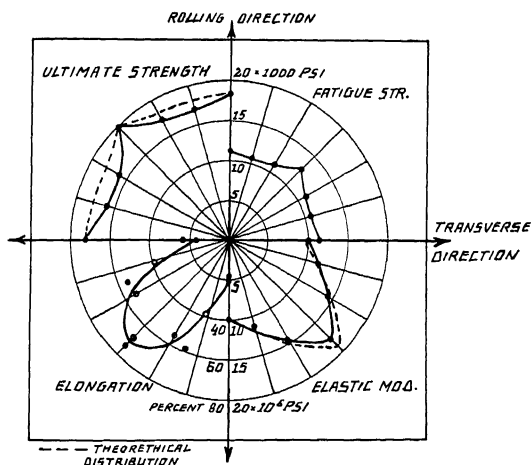


FIG. 18.—DIRECTIONALITY OF VARIOUS PROPERTIES OF ANNEALED COPPER SHEET WITH "CUBIC" FIBER STRUCTURE.

Cubic axes parallel to rolling, transverse and normal directions.

aggregates, much less success has been achieved with the conditions of rupture. It appears, from extensive experiments by Schmid³⁶, on single crystals of the brittle type, that cleavage occurs if the normal stress on the crystal plane that functions as the cleavage plane attains a critical value. However, this simple relation does

ductile metals do not develop cleavage fractures but fail in tension by a process similar to the necking of the polycrystalline metals (Fig. 8). At the present time the factors responsible for this type of failure and the conditions that govern the failure of metals in commercial working are not known.

The following parts of this lecture will, for this reason, deal only with the principal factors that influence the plastic flow in commercial working of metals.

curve describes the resistance of a metal to any type of strain such as tension, compression, shear or combinations of them. It is, also, possible to derive from such crys-

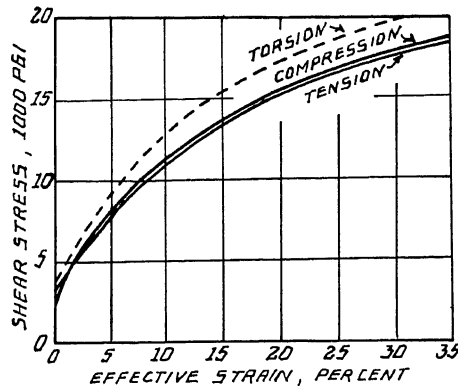


FIG. 19.—STRAIN-HARDENING OF COPPER IN TENSION, COMPRESSION AND TORSION (ROS AND EICHINGER).

STRAIN-HARDENING OF METALS

One of the unsolved mysteries of metallurgy is the source of the strain-hardening occurring during cold-working. This immensely important property, which is characteristic not only of metals but also of other crystalline matter such as rock-salt,⁴⁸ has not yet been given a convincing theoretical explanation. Many metallurgists fear that the tools available are not sensitive enough to discover the source of the strain-hardening and that the most modern and unfortunately least lucid physical conceptions will be required to solve this problem.

As previously discussed, the capacity for strain-hardening is an inherent property of any single metallic crystal (Fig. 15). It is well known that strain-hardening is retained only at comparatively low temperatures. Heating eliminates this effect and approximately reproduces the original softness.

It has been also mentioned that the strain-hardening of single crystals of a specific metal can be represented by a characteristic stress-strain curve. This

tallographic data a corresponding stress-strain curve describing the behavior of a polycrystalline aggregate subjected to any type of strain.

This practically important problem attracted the interest of the metallurgist in an early stage in the development of metallurgical science. Ludwik⁴⁹ proposed that the extent of shear along the continuously changing plane of maximum shear stress determines the magnitude of strain-hardening. Thus, the stretching of a certain initial length (l_0) to a final length (l_1) will produce the same strain-hardening as the compression of an initial height (l_1) to a height (l_0). Ludwik also introduced a logarithmic strain function, the "effective strain":

$$\epsilon = \log_e \frac{l_1}{l_0} = -\log_e \frac{l_0}{l_1}$$

which represents the shear strain of a polycrystalline material. The stress-strain diagrams¹⁵ of a metal both in tension and in compression plotted with the effective strain as abscissa are identical (Fig. 9), and the same is true for the stress-strain

diagram in torsion (or shear) if it is considered that the flow stress is 10 to 15 per cent higher in torsion than in tension or compression, as previously discussed (Fig. 7).

The commercial working processes may be either of the tension, compression or shear type, or of a combination type. As the volume in plastic deformation remains virtually constant, one principal strain is either tension or compression, while the other two have the opposite sign. The strain-hardening is determined by the strain that is different from the other two with regard to its sign, such as the stretching in drawing or the reduction of thickness in rolling.

While these relations offer at least simple approximations, which may be useful in practice, attempts have been made also to develop strain functions that closely agree with the experimental results. Among these functions, the so-called "octahedral shear" developed by Nadai⁵⁰ has attracted particular interest. However, as previously mentioned, a correlation of the strain-hardening of polycrystalline aggregates with that of single crystals has not yet been achieved in a general manner.

EFFECTS OF TOOL CONTACT AND FRICTION ON PLASTIC FLOW

Any attempt to apply the described fundamental conceptions to plastic flow encounters the principal difficulty that the flow in a commercial working process is not uniform.⁵¹

This discussion will not consider any chemical source of nonuniformity, such as that represented by segregations or "dendrites," but assumes that the metal subjected to the working process is homogeneous. Nevertheless, it is usually observed that various parts of an article have different properties, particularly the surface and the core. This may be caused by various factors such as:

1. The localized action of the tools.

2. The presence of friction between metal and tool.

3. The heat developed by deformation and friction.

4. Impacts associated with high-speed working.

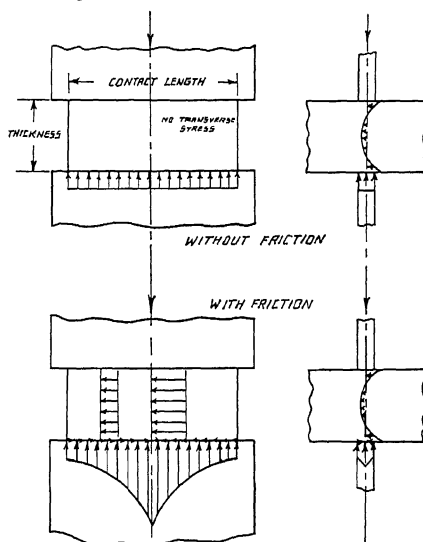


FIG. 20.—DIAGRAMMATIC REPRESENTATION OF EFFECTS OF CONTACT LENGTH AND FRICTION IN FORGING.

Little work has been done so far toward analyzing working processes in these respects, and the following remarks are therefore speculative.

The effect of the tools in working a metal depends particularly upon the size of the working surface of "area of contact." While it is impossible as yet to develop quantitative relations, it appears that the ratio (l/h) between the length of contact (l) in the principal direction of flow and the thickness (h) of the metal is the determining factor. A thin bar will flow uniformly under the action of large dies (Fig. 20), developing mainly compression stresses in the direction perpendicular to the die surface. However, a bar subjected to the localized attack of narrow tools (Fig. 20) will be plastically deformed only in the vicinity of the contact area. A load concentrated at a single point creates a very

nonuniform stress distribution and compression or tension may be present at a specific point in both the axial and the

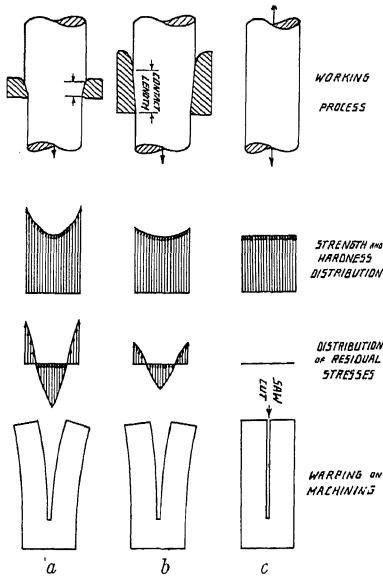


FIG. 21.—EFFECTS OF CONTACT LENGTH IN DRAWING ON PROPERTIES OF PRODUCT.

- a, drawing with large die angle.
b, drawing with small die angle.
c, tension (stretching).

transverse directions. Thus, with a given metal thickness, the deviations from uniformity will increase with decreasing contact length. This conclusion has been confirmed for any type of working process, and has been thoroughly examined for wire drawing.⁵² A wire drawn through a wide-open die (Fig. 21) having a short contact length will develop a nonuniform stress and strain distribution. The strength of the surface layers will be considerably higher than that of the core, and high residual stresses will be retained, which will cause considerable distortion during machining. On the contrary, a wire drawn with an acute-angle die will be in every respect more uniform, approaching the condition of a uniformly stretched tensile-test bar.

The effects of friction on plastic flow also primarily depend upon the ratio of contact

length to metal thickness (Fig. 20). With a short contact length little friction is present and its effect mainly consists of accentuating the nonuniformity of the stress and strain states. With a large contact length, however, two types of friction effects are developed. First, the friction acting along the contact length and opposing the metal flow may reach a high force. With very thin metal, as in rolling thin strip or die forging with a thin flash, the friction may completely prevent any flow, and the equipment will fail before the metal is displaced. Under less extreme conditions, a high transverse pressure is created, and consequently a high pressure is required to deform the metal. This, however, corresponds to the superposition of hydrostatic pressure and results in the beneficial effect of increasing the ductility, as previously discussed. This second effect is valuable in working sensitive metals.

SPEED AND IMPACT EFFECTS

One of the least analyzed and explained factors in mechanical working is the working speed. It has been recognized that the following effects can be influenced by the velocity of deformation: (1) the properties of the metal, (2) the impact effect, or stress and strain concentration in the metal adjacent to the tool, (3) the heat development and dissipation.

The metal properties depend only slightly upon the working speed in cold-working, while in hot-working the flow resistance of the metal increases considerably with increased working speed. The displacement of the cold-working range to higher temperatures by an increased rate of working^{51,53} is of practical importance and results in the restriction of the range of hot-working temperatures. This explains the benefit derived from the slow working of many alloys, such as high-alloyed steels and magnesium alloys. The peculiar and unexplained brittleness present in some alloys, for instance, the alpha brasses, is

found at different temperatures, depending upon the rate of strain.⁵⁴ Another unusual phenomenon is the increase of the yield point jog and of the associated tendency of

ferred through the metal to the various sections being worked. In compression-type working, such as is represented by the upsetting of a blank (Fig. 22), the main

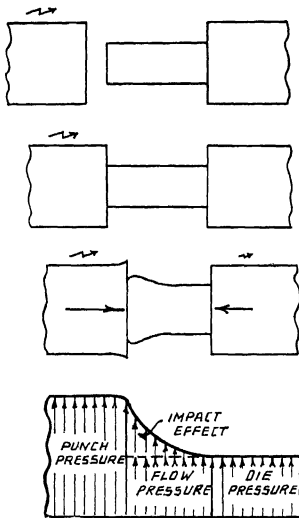


FIG. 22.—DIAGRAMMATIC REPRESENTATION OF EFFECT OF IMPACT ON STRAIN AND STRESS IN UPSETTING.

stretcher strain formation by increasing the speed of cold-working low-carbon steels.⁵⁵

In commercial practice it is widely recognized that it is extremely important to overcome the impact effects.⁵¹ The impact appears to be the primary factor limiting the working speed in many commercial processes.

The impact effect may be fundamentally defined as the additional stresses and strains resulting from deviations from static equilibrium. A body is in static equilibrium when it is at rest or when it is moving with uniform velocity. Accelerations and decelerations, however, such as those particularly present at the beginning of a working process, will result in stresses in addition to those required to overcome the flow resistance of the metal. This impact effect is more important in the tension-type than in the compression-type working processes. Generally, the acting force must be trans-

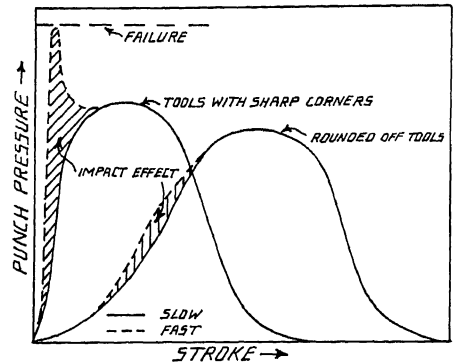


FIG. 23.—DIAGRAMMATIC REPRESENTATION OF EFFECTS OF TOOL DESIGN AND SPEED IN WORKING ON FORCE-STROKE DIAGRAM IN DEEP DRAWING.

effect is the formation of increased stresses and strains adjacent to the tool that strikes the metal at high speed. The capacity of most metals to "take" such an impact blow is not restricted; therefore the blank will be only somewhat less uniformly deformed at high rates of working than at lower ones. On the contrary, in tension-type working, as in drawing rod, wire and tubing, and also in rolling sheet under tension, the strength of the metal limits the maximum force that can be transferred from the acting tool to the section being worked. Therefore, impact consumes a portion of the force that could be utilized for an increased reduction to be performed in a single operation.

The methods being used to decrease impact effects are mainly of two types. One method reduces the speed of the acting tool during the starting period, either directly by the use of direct current motors or indirectly by inserting "soft" members, which yield before the maximum force is developed. The other method is to design the tool in such a manner that the metal itself acts as an impact cushion. For example,

in deep drawing (Fig. 23) sharp-cornered tools almost immediately create the maximum metal resistance and the impact effect, while generously rounded off tools permit the metal to move before developing a high flow and impact resistance. As previously discussed, the impact effect is mainly restricted to the region where tools and stock strike each other (Fig. 22). The particles in this contact area suffer the highest impact acceleration, but this acceleration is rapidly reduced as the distance from the contact area increases. The stresses set up in the metal and in the tools are of two types, the plastic or elastic resistance of the metal plus an additional stress proportional to the acceleration. From this feature of any impact effect, the interesting conclusion can be drawn that the stock should be placed in the parts of the dies that are particularly highly stressed, while the less strained part should be the impacting tool.

Regarding the effects produced by the heat developed during working, it should be recalled that the mechanical work consumed in both cold-working and hot-working is almost entirely converted into heat.⁵⁶ This heat comes from two sources, a uniform or volume part originating from the strain within the metal and a surface portion resulting from the friction. The corresponding increase in temperature is determined by the dissipation of the heat mainly due to conduction through the tools and the metal itself. Therefore, the faster the total volume of metal is being worked and the shorter the time the tools remain in contact with the metal after working, the higher will be the increase in temperature of the metal, other factors being equal. This temperature increase can assist the working, as in impact extrusion, or it can cause difficulties, as in the hot-working of a metal with a narrow working temperature range. Apparently little has been done as yet to apply the laws of heat transfer to metal-working problems.

CONCLUSION

In concluding, may I be permitted to say a few words as to the probable future development of the knowledge of the plastic deformation and rupture of metals. As a science, this branch of metallurgy is most akin to the theory of elasticity. However, the complex theory of elasticity is based on a minimum number of basic assumptions, incorporated in Hooke's law, and on the knowledge of a few properties of the material; i.e., the elastic constants. Other factors, such as the deviations from Hooke's law, or imperfections of elasticity, are of minor importance and do not diminish the tremendous practical usefulness of the theory of elasticity. On the contrary, the plasticity and rupture of metals depend, as discussed, upon numerous fundamental factors and also upon numerous specific metal properties. Therefore, extensive research combining carefully balanced theoretical and experimental work will be necessary to achieve further success. Unfortunately, rather sensitive, complex and expensive experimental equipment is required for this work, and as a consequence the progress in this particular field of metallurgy will be rather slow.

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Internal Friction of Single Crystals of Copper and Zinc

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(New York Meeting, February 1941)

THE internal friction of single crystals of metals is affected markedly by a variety of factors, which, according to the literature, are without influence on the internal friction of polycrystalline metals at strain amplitudes less than 10^{-5} . For example, the internal friction of a suitably oriented zinc single crystal is multiplied by a factor of 100 when the vibration amplitude is slightly increased, and the internal friction of a copper crystal is markedly increased by the application of a stress of 30 lb. per sq. in. for one minute. In this paper it will be shown that these, together with the other phenomena associated with the damping of mechanical vibrations in metal single crystals, can be satisfactorily explained, at least qualitatively, in terms of an atomic mechanism that has been proposed for quite another purpose—that of accounting for slip in metals. The extraordinary agreement between the observed behavior of the metal single crystals and the behavior that could be predicted on the basis of this atomic mechanism leads to the belief that the latter is probably essentially correct. If this is so, it follows that valuable information about the slip process in metals may be gained from measurements of internal friction on single crystals.

In this paper the results of the only study to date on the damping of mechanical vibrations in single crystals of metals will be presented.

EXPERIMENTAL PROCEDURE

The internal friction of a material is a measure of the rate at which the energy of mechanical vibrations is converted into heat. The measure of internal friction used in the present paper is the decrement Δ , which is defined as the fraction of the energy of vibration lost per half cycle. The measurements described here were made for longitudinal oscillations at a frequency of 33.5 kc. for the copper crystals, and at a frequency of 39 kc. for the zinc crystals.

The method used is that of the composite piezoelectric oscillator. The single-crystal specimens are in the form of circular cylinders $\frac{1}{4}$ in. in diameter and $1\frac{1}{2}$ to $2\frac{1}{2}$ in. long. The crystal rods are waxed in a V-block and sawed to the proper length with a fine jeweler's saw. The ends of the specimen are ground flat, and one end is cemented with a very thin film of beeswax and rosin to the end of an x-cut quartz rod which is $\frac{1}{4}$ in. in diameter and 3 in. long. The length of the specimen rod is determined by the condition that its natural frequency for longitudinal vibration be the same as that of the quartz rod, within 0.5 per cent. The lengths of the specimens are thus different for different orientations of the cylinder axis with respect to the crystallographic axes. When the specimen and quartz rods are thus matched in frequency the adhesive is at a node of stress, and it has been shown experimentally that under these circumstances

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the energy dissipation in the adhesive material is negligibly small.

This composite oscillator is mounted in a vacuum either horizontally or vertically, but in either case it is supported by fine wires at nodes of displacement. Two brass electrodes are placed on either side of the quartz rod at the ends of the electric axis (in an x-cut quartz rod the electric axis is perpendicular to the axis of the rod). The composite oscillator is excited to longitudinal vibration by placing on these electrodes an alternating electromotive force of appropriate frequency. A composite piezoelectric oscillator is shown schematically in Fig. 1.

The measurement of the rate at which energy is dissipated in the composite oscillator is thus reduced to an electrical measurement, and is carried out by connecting the electrodes in one arm of an alternating-current bridge. The decrement of the specimen rod is calculated from data on the variation with frequency of the equivalent electrical impedance of the composite oscillator in the neighborhood of the resonance frequency, and from a knowledge of the decrement of the quartz rod.

A very important feature of this method of measurement is that it is possible to measure with precision the amplitude of stress in the specimen, even though it be as small as 0.01 lb. per sq. in. This is done by measuring the absolute value of the energy dissipated per cycle in the specimen. From this and the decrement one can calculate the total energy stored in the mechanical vibrations, and thus the amplitude of stress in the specimen. The amplitude of oscillation at which the measurement is made is varied by changing the voltage applied to the bridge circuit, and hence the voltage on the electrodes of the quartz oscillator.

A complete description of the method of the composite piezoelectric oscillator (which was developed by Prof. S. L. Quimby, of Columbia University, and his students) and

of the manner in which it has been modified for measurements of damping in metal single crystals may be found in an earlier paper.¹

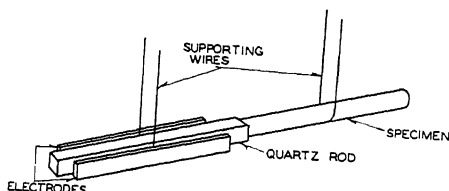


FIG. 1.—COMPOSITE PIEZOELECTRIC OSCILLATOR MADE BY CEMENTING QUARTZ AND SPECIMEN RODS END TO END, SUSPENDED BY FINE WIRES IN AN EVACUATED CONTAINER.

SPECIMEN MATERIAL

The copper crystals on which the measurements were made were grown from Chile copper, which contains 99.998 per cent Cu. It was obtained in the form of disks $\frac{1}{4}$ in. in diameter and $\frac{1}{16}$ in. thick and was melted in a graphite crucible in a vacuum induction furnace and cast into rods. These rods were converted into single crystals by the method of gradual solidification from the melt in a vacuum furnace similar to the one described by Nix.²

The zinc crystals were grown by the method described by Miller³ from c.p. zinc (99.999 per cent Zn) supplied by the New Jersey Zinc Co. The principal features of this method of production of single crystals are as follows: The zinc is melted in a Pyrex flask and thoroughly degassed in a vacuum. It is then cast in cylindrical molds of Pyrex tubing, which have been thoroughly cleaned and coated with colloidal graphite, to prevent the zinc from sticking to the glass. The molds containing the polycrystalline zinc are packed in a large test tube in Sil-O-Cel and lowered through an electric furnace at the rate of $\frac{1}{4}$ in. an hour.

After growth, the crystals were annealed for 2 hr. and cooled slowly to room temperature.

¹ References are at the end of the paper.

RESULTS ON COPPER

If measurements are made on a copper crystal immediately after it has been

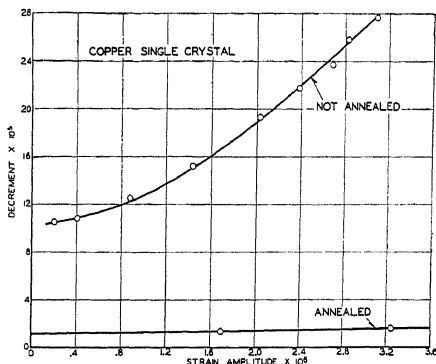


FIG. 2.—INTERNAL FRICTION OF COPPER SINGLE CRYSTAL DECREASED BY ANNEALING TWO HOURS AT 500°C.

Upper curve shows dependence of decrement on strain amplitude before annealing; lower curve, after annealing.

sawed and its ends ground, it is found to have a rather high internal friction, which varies markedly with the amplitude of the oscillations, as shown by the upper curve in Fig. 2. If the crystal is then annealed for 2 hr. at 500°C., and the measurements repeated, the decrement is much lower than before annealing, and, moreover, varies much more slowly with the amplitude of oscillation. This behavior is shown in the lower curve in Fig. 2. But even after annealing there is still a measurable dependence of the decrement on the amplitude; in Fig. 3 the lower curve of Fig. 2 is replotted on a different scale, and carried out to larger amplitudes. The decrement measurements were carried out to larger amplitudes on the annealed crystal than on the unannealed crystal, because, for a given maximum voltage on the quartz oscillator, the amplitude of oscillation is inversely proportional to the decrement.

It is evident from the curves of Fig. 2 that the internal friction of a copper crystal is sensitive to handling. In order to investigate this effect quantitatively, the following experiment was carried out. First, a

small compression machine was constructed (Fig. 4). This device was carefully made so that a specimen could be compressed be-

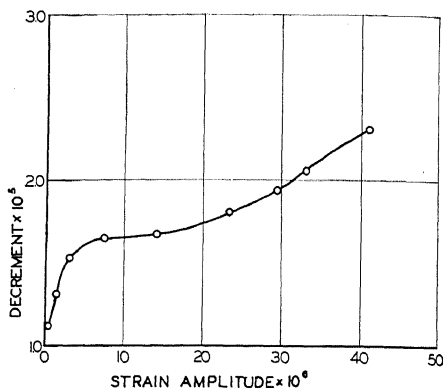


FIG. 3.—LOWER CURVE OF FIG. 2 ON EXPANDED SCALE.

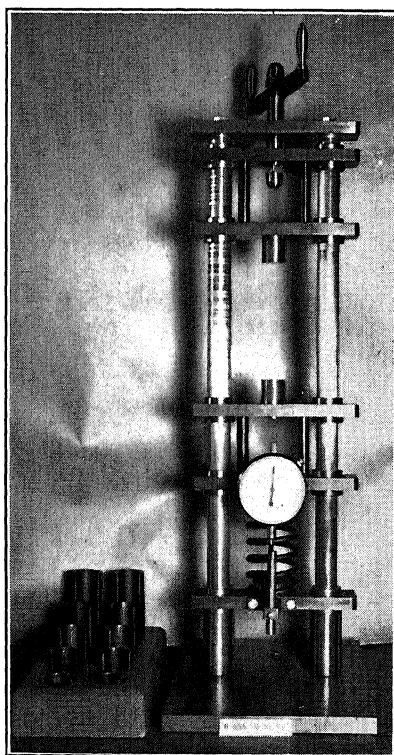


FIG. 4.—DEVICE FOR APPLYING COMPRESSIVE STRESSES TO SINGLE-CRYSTAL RODS.

tween two plates accurately parallel to one another, and perpendicular to the direction

of motion. The load was measured by the amount the spring supporting the lower sliding member was compressed, by using a sensitive dial gauge.

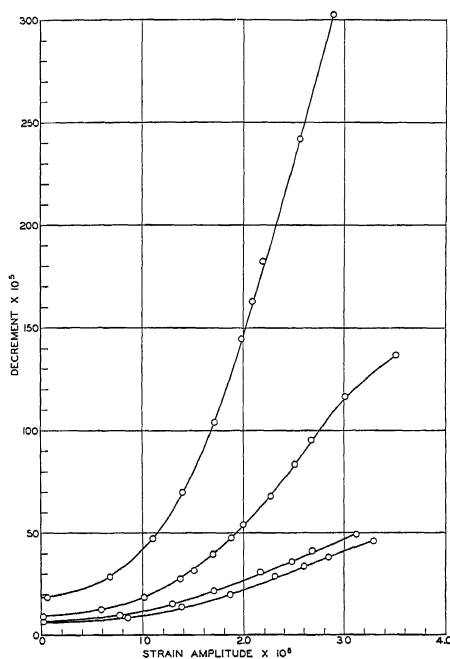


FIG. 5.—INTERNAL FRICTION OF COPPER CRYSTAL INCREASED BY APPLYING SMALL STRESSES TO IT FOR ONE MINUTE

Lowest curve was obtained before stressing crystal; next above it after applying 60 lb. per sq. in.; the third after 120; the fourth after 150 lb. per sq. inch.

Using this device, a single crystal of copper was successively subjected to loads of 3 lb., 6 lb., and $7\frac{1}{2}$ lb., each for one minute. The diameter of the crystal was $\frac{1}{4}$ in., so these loads produced compressive stresses in the crystal of 60, of 120 and of 150 lb. per sq. in. Before and after each stressing of the crystal its decrement was measured as a function of the amplitude of oscillation, and the four curves obtained are shown in Fig. 5. The lowest curve represents the first measurement, and the other three follow in order; each application of stress produced an increase in the internal friction. No change in the length

of the specimen was observed. With this method a change of one part in 30,000 could have been detected by the resulting change in the resonant frequency.*

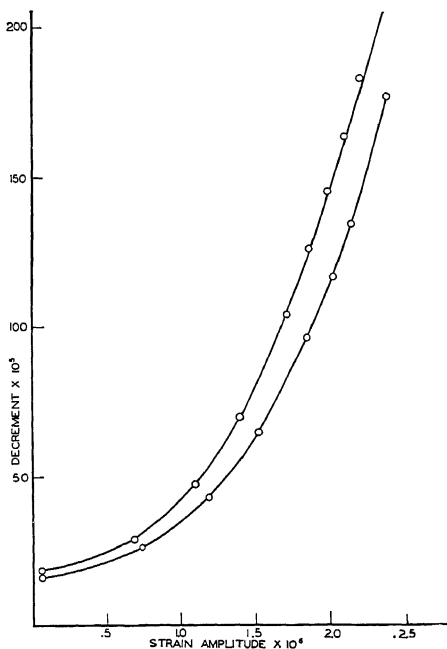


FIG. 6.—INTERNAL FRICTION OF COPPER CRYSTAL AT 23°C. (UPPER CURVE) AND AT 0°C. (LOWER CURVE).

Preliminary measurements have also been made of the temperature dependence of the internal friction of copper crystals in the neighborhood of room temperature. The data presented in Figs. 2, 3 and 5 were obtained at 23°C. In Fig. 6, the top curve of Fig. 5 is replotted, together with a similar curve representing measurements made on the same specimen at 0°C. immediately after the 23°C. run. It is to be noted that the decrease in the decrement resulting

* It is possible that the length of the crystal was decreased by more than 0.003 per cent by the stressing but that the Young's modulus of the crystal was simultaneously lowered (the percentage decrease in Young's modulus being twice the percentage decrease in length). This possibility could be investigated by stressing the crystal in tension.

from this lowering of the temperature is only about 20 per cent.

In addition to the decrement measurements, data were obtained on another

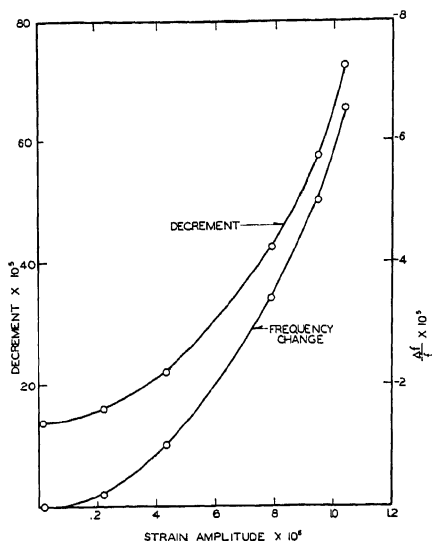


FIG. 7.—DECREMENT AND FRACTIONAL CHANGE OF RESONANCE FREQUENCY OF LONGITUDINAL VIBRATION OF COPPER CRYSTAL ROD PLOTTED AS FUNCTIONS OF STRAIN AMPLITUDE.

phenomenon, the variation of the *resonant frequency* with the amplitude of oscillation. The resonant frequency is defined as the frequency of driving voltage that produces the maximum amplitude of oscillation. It is determined by the length, density, and Young's modulus of the specimen, except for a small correction depending on the specimen diameter. It was found that as the amplitude of oscillation was increased the resonant frequency of the single-crystal rod decreased by a small amount, never more than about 0.01 per cent. In Fig. 7, typical curves showing the dependence of decrement and resonant frequency on vibration amplitude are reproduced. The decrease in the resonant frequency as the amplitude is increased is plotted in terms of the fractional change in frequency,

$\delta f/f$, from the resonant frequency at a very small amplitude.

RESULTS ON ZINC

The experimental data on single crystals of zinc have been previously published,¹ but they will be reviewed here so

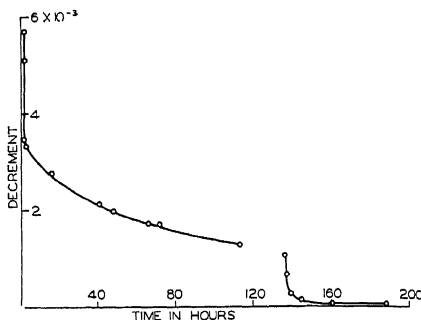


FIG. 8.—DECREASE IN INTERNAL FRICTION OF ZINC CRYSTAL WITH TIME AFTER MOUNTING.

All these measurements were made at amplitudes so small that the decrement was independent of the amplitude. The gap in the curve represents a one-hour anneal at 250°C.

that they may be compared with the results on copper.

As in the copper crystals, the internal friction of zinc crystals was high immediately after the process of sawing the crystal, if no annealing process intervened. But an additional phenomenon was then observed; while the specimen was mounted in the apparatus at room temperature, its decrement decreased, at first very rapidly, and then more slowly, in the manner shown in Fig. 8. After 4 days, corresponding to the break in the curve, the composite oscillator was removed from the apparatus and the zinc crystal annealed for 1 hr. at 250°C. It was then replaced in the apparatus and the measurements continued. It is remarkable that the decrement at the beginning of this series of measurements was almost a thousand times the final value, which was 1.5×10^{-5} . All of these measurements were made at very small vibration amplitudes—so small that decreasing the amplitude by 50 per cent did not produce any measurable change in the decrement. Because of this dependence of the decrement of zinc crystals on the time

after mounting, all the measurements to be described were made several days after the mounting process, when the decrement had reached a steady value.

It was also found that the properties of the crystals are changed by the oscillations themselves. Fig. 9 shows the way in which the internal friction depends on the length of time the crystal is oscillated. After 10 min., or 25 million cycles, a sensibly constant value is reached, so all readings were taken after this steady state was attained. At very small amplitudes this effect was not observed.

Another complication in making measurements of the internal friction of zinc crystals is that the values obtained depended on the *order* in which the measurements are made. This phenomenon is illustrated in Fig. 10. Starting the measurements at the smallest vibration amplitude and making measurements at successively increased amplitudes, the lower branch of the curve was obtained. If the measurements at the lower amplitudes were then repeated, values of the decrement higher than before were obtained, corresponding to the upper branch of the curve.

Finally, it is found that there is a large difference in the damping properties of zinc crystals whose orientations of the cylinder axis with respect to the hexagonal axis are different. Fig. 11 shows the dependence of decrement on strain amplitude for several crystals of various orientations. The angle θ is the angle between the cylinder axis and the hexagonal axis.

As with copper, the resonant frequency of zinc crystals decreases as the vibration amplitude is increased. In Fig. 12 the fractional decrease in resonant frequency is plotted as a function of the strain amplitude in the specimen for the same crystals whose decrements are plotted in Fig. 11.

This change in the resonant frequency can be correlated with the decrement changes. If the data of Figs. 11 and 12 are combined by plotting the decrement

against the change in the resonant frequency (Fig. 13), a straight-line relationship is found. This means, then, that for each of these crystals the ratio $r =$

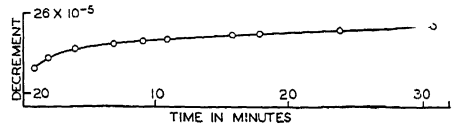


FIG. 9.—DECREMENT OF ZINC CRYSTAL ROD INCREASES WITH TIME WHILE OSCILLATING.

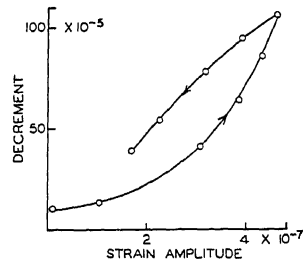


FIG. 10.—DECREMENTS MEASURED WHEN STRAIN AMPLITUDE IS INCREASED BY STEPS ARE SMALLER THAN THOSE WHEN STRAIN AMPLITUDE IS SUBSEQUENTLY DECREASED.

$\left(\Delta \div \frac{\delta f}{f}\right)$ is a constant independent of the strain amplitude. The values of r for the different crystals are given in Table I.

TABLE I.—Values of Ratio $r = \Delta \div \frac{\delta f}{f}$ for

| Different Zinc Crystals | |
|-------------------------|------|
| θ° | r |
| 20.0 | 2.8 |
| 61.2 | 10.3 |
| 61.5 | 11.0 |
| 74.5 | 9.0 |
| 88.0 | 1.1 |

An important characteristic of any dissipative process, a knowledge of which is essential to an investigation of the origin of the dissipation, is the dependence on frequency. Zinc single crystals are so sensitive to handling and other influences that are difficult to control that it is necessary that the measurements at the different frequencies be made on the same specimen,

and with all other factors kept constant. This can be done by making measurements on the same composite oscillator, but at its second harmonic. A typical result is given

the hexagonal axis, and the smallest tension will be required to produce slip in a single-crystal rod if the basal plane makes an angle of 45° with the axis of the rod

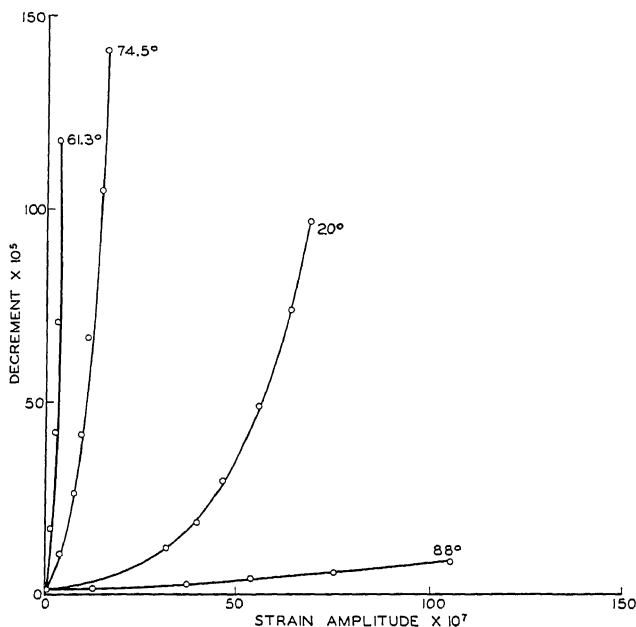


FIG. 11.—VARIATION OF DECREMENT WITH STRAIN AMPLITUDE IN ZINC CRYSTALS WHOSE CYLINDER AXES MAKE VARIOUS ANGLES θ WITH HEXAGONAL AXIS.

in Fig. 14, which shows that the decrement for a given strain amplitude is approximately inversely proportional to the frequency.

DISCUSSION OF RESULTS

There are two striking differences between the behavior of copper crystals and that of zinc crystals. One is that there is no analog of Figs. 8 and 9 for copper, and the other is that only in the case of zinc is there a marked dependence of the decrement on the orientation of the crystal. This second difference is very suggestive, if we keep in mind that the slip properties of the two metals differ in just the same way. Zinc, with its hexagonal crystal structure, slips at room temperature only on the basal plane perpendicular to

The crystal structure of copper, on the other hand, is face-centered cubic, and it will slip on all the (111) planes. For any orientation of the rod one of these planes will lie at or near the 45° position.

Further evidence that the damping of mechanical vibrations in zinc crystals results from their plasticity is afforded by the observed dependence on frequency. An inelastic deformation proportional to the length of time the stress is applied gives rise to a decrement inversely proportional to the frequency, like that observed for zinc crystals.

The conclusion is that the phenomena of slip and the dissipation of vibrational energy are related. Before discussion of this relationship, let us digress to consider the dislocation theory of slip in metals.

DISLOCATION THEORY OF SLIP*

Metals are deformed plastically by the processes of slip and of twinning. By "slip" is meant the relative displacement

posed that the elementary unit of slip is the relative displacement of two planes in the crystal, each plane moving as a unit. An estimate of the shearing stress neces-

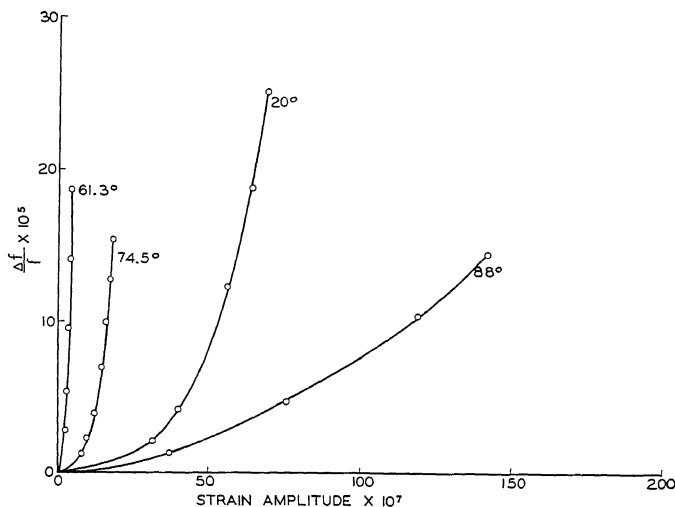


FIG. 12.—FRACTIONAL VARIATION OF RESONANCE FREQUENCY WITH STRAIN AMPLITUDE IN ZINC CRYSTALS WHOSE CYLINDER AXES MAKE VARIOUS ANGLES θ WITH HEXAGONAL AXIS.

of two planes in a crystal lattice by a distance equal to some integral multiple of the distance between two equilibrium positions for atoms in that plane. After slip has taken place, the atoms are in new equilibrium positions, and the ideal lattice structure is preserved. Slip may occur simultaneously on a great many parallel crystallographic slip planes. The slip plane in a metal usually is the plane that is most thickly populated with atoms, and the slip direction is parallel to the line in the plane that has the greatest atomic density. Visual evidence for the existence of slip planes is given by the formation of glide ellipses on the surface of a plastically deformed single-crystal rod—ellipses formed by the intersection of the cylindrical surface and the plane of slip.

Since the slip process has such a definite crystallographic nature, it might be sup-

sary to produce such a motion can be made easily. When the plane is just halfway between two equilibrium positions the shear is approximately $\frac{1}{4}$, and the shearing stress is roughly $\frac{1}{4}G$, where G is the shear modulus. An average value of G for metals is 5 million lb. per sq. in., so the calculated stress necessary to produce slip is about 1 million lb. per sq. in. In order to account for the discrepancy between this figure and the observed values, which are in the neighborhood of 100 lb. per sq. in., slip mechanisms have been proposed, according to which slip takes place over only a small part of the slip plane at once. One way in which this can happen is through the motion of dislocations through the crystal lattice. A dislocation, which is a particular type of imperfection in the regularity of the crystal lattice, is illustrated in Fig. 15. When such a dislocated region moves from one side of the crystal to the other, the two atomic planes undergo a relative dis-

* A good review of this subject appears in chapter V of "Elasticity, Plasticity, and Structure of Matter" by R. Houwink. Cambridge Univ. Press, 1937.

placement of one lattice distance. It has been illustrated by Taylor⁴ that the atoms in the dislocation are bound relatively loosely to their positions of equilibrium;

mobility of the dislocations will be enhanced, and some of them will migrate out of the crystal, or will coalesce with dislocations of the opposite sign. After the

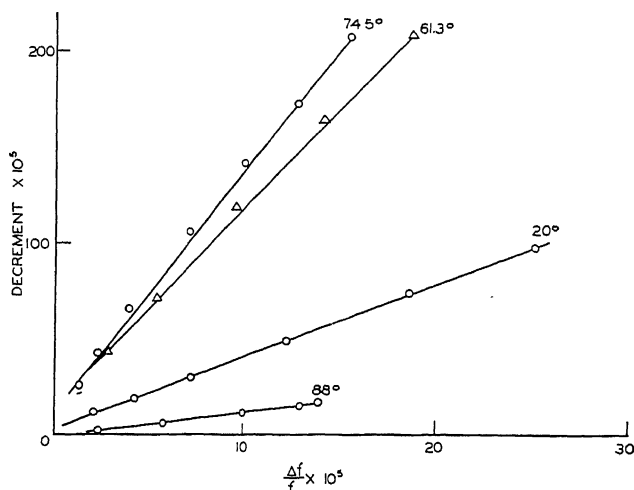


FIG. 13.—COMBINATION OF DATA PLOTTED IN FIGS. 11 AND 12. Shows that ratio of decrement to fractional change in frequency is constant.

for this reason the dislocation can be moved through the crystal by a very small stress σ_1 . In general, the stress σ_2 required to produce the dislocation will be larger than σ_1 , and will be the stress it is necessary to apply to the crystal in order to make it slip. Let us now apply these ideas to the interpretation of the results on the damping of mechanical vibrations in metal crystals.

INTERNAL FRICTION OF METAL CRYSTALS

Since no actual crystal is perfect, every crystal will contain a certain number of dislocations, depending on how much plastic deformation it has undergone. Under the influence of an oscillating stress, these dislocations will move back and forth in the crystal and thereby dissipate the energy stored in the oscillations. In moving the dislocations, the external stress will be aided by the random fluctuations in stress in the crystal that arise from the thermal motions of the atoms. If the crystal is raised to an elevated temperature, the

crystal has been brought back to room temperature, the number of dislocations in the crystal will be smaller and the internal friction lower. This prediction is verified by Fig. 2 for copper and by Fig. 8 for zinc. For zinc, we find that the dislocations migrate out of the crystal at a finite rate at room temperature.

As the converse of annealing, deforming the crystal plastically increases the density of dislocations in the crystal; this should increase the internal friction. Fig. 5 gives the result of such an experiment on copper, and shows that the internal friction is raised by slight amounts of cold-work. With zinc, it is not necessary to apply such large shearing stresses to the slip plane; the internal friction is increased measurable amounts by the alternating stress associated with the vibrations when this stress is as low as 1 lb. per sq. in. (Figs. 10 and 11).

Any theory of the dissipation process in these metal crystals that is worth while must offer an explanation of the depend-

ence of the decrement on the amplitude of vibration. This is done by the mechanism of the motion of dislocations in the following way: The stress σ_1 , which is required

decrement-amplitude curve does become flatter at strain amplitudes above 4×10^{-6} .

This discussion applies to both copper and zinc, but for zinc there is an additional

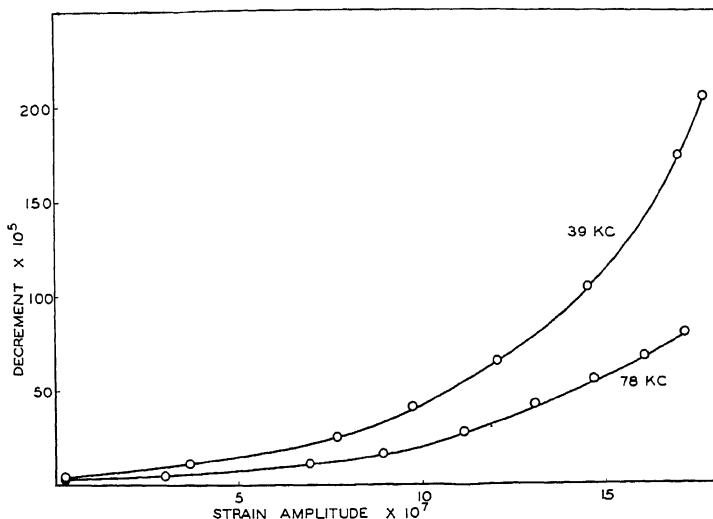


FIG. 14.—INTERNAL FRICTION OF ZINC CRYSTALS IS VERY NEARLY INVERSELY PROPORTIONAL TO FREQUENCY AT ALL STRAIN AMPLITUDES.

Vibration frequency for data of upper curve is 39 kc.; of lower curve, 78 kc.

to move a dislocation through the lattice, is in general larger than the oscillating stress associated with the vibrations. Motion of the dislocations is made possible by the thermal vibrations of the atoms in the lattice, which may be regarded as producing fluctuations in the stresses that act on the dislocations. As the amplitude of vibration is increased, the additional stress that must be supplied by the thermal motions in order to make the total stress acting on the dislocations equal to σ_1 becomes smaller, so the rate of motion of the dislocations is greatly increased. If this explanation is correct, it would be expected that the dependence of decrement on stress amplitude would not be so great if the vibrational stress exceeds σ_1 . This prediction may be compared with the data shown in Fig. 3, which shows the result of measurements at relatively large amplitudes and demonstrates that the

cause of the amplitude dependence. As the amplitude is increased, more dislocations are produced in the zinc crystals, which

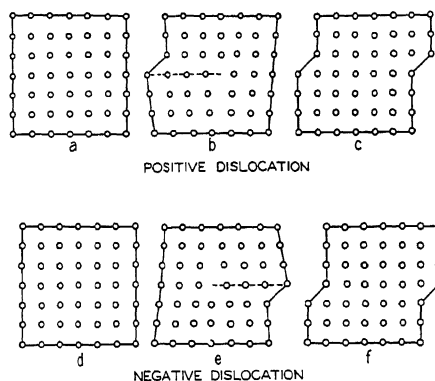


FIG. 15.—FORMATION AND PROPAGATION OF A DISLOCATION (AFTER TAYLOR).

gives rise to a rapid increase in their damping even up to the largest amplitudes of oscillation.

Another feature of the measurements, which can be understood in terms of the dislocation picture, is the change of resonant frequency produced by increasing

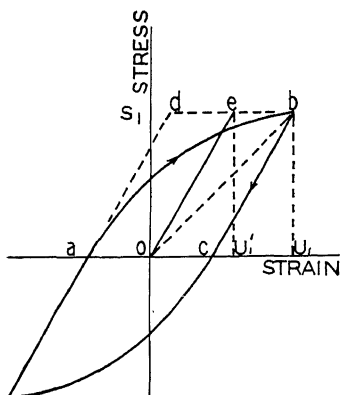


FIG. 16.—SUGGESTED FORM OF STRESS-STRAIN DIAGRAM FOR SINGLE METAL CRYSTALS.

the amplitude of vibration. It is important to realize that this effect could not be produced by an inelastic strain rate uniquely determined by the stress; i.e., independent of the time. It can be produced only by some process that gives rise to an asymmetrical stress-strain loop. Such a process is provided by the motion of dislocations, at least under certain circumstances. If it is assumed that during the quarter cycle in which the stress increases from zero to its maximum value a large proportion, say 50 per cent, of the available dislocations are moved until they are stopped by some obstruction such as an impurity atom, in the next quarter cycle fewer dislocations are moved, as most of them will have been "used up." This situation has been idealized in Fig. 16. The line *oe* represents purely elastic behavior and gives the actual stress-strain relationship at very small stresses. At larger stresses an inelastic strain is produced as the result of the motion of dislocations—represented by the strain *db*. Assume now that as the stress decreases no further motion of dislocations takes place, and part *bc* of the

loop is simply an elastic contraction. It must be remembered that Fig. 16 is not drawn to scale. The actual plastic strain, shown by the intercept *ac*, is not larger than one-thousandth the strain amplitude, shown by the abscissa *U/1*. The stress-strain loop is extremely narrow, and the slope of the line *ob* may be taken as the effective Young's modulus. It can be shown that for the loop illustrated in Fig. 16 the ratio *r* of decrement to fractional change in frequency lies between 4 and 8, depending on the shape of the curve *ab* and is independent of the amplitude of the stress. This result is in general agreement with the data of Table 1.

SUMMARY

1. Measurements of the internal friction of single-crystal rods of copper and zinc have been made for longitudinal oscillations at frequencies of 33.5 and 39.0 kc., respectively. The measurements on zinc were also made at 78.0 kilocycles.

2. By careful annealing, the decrements of the single-crystal rods may be made as low as 1×10^{-5} .

3. The internal friction of single crystals of copper and zinc is increased by even very small amounts of cold-work.

4. The decrements of all the crystals vary markedly with the amplitude in the range of "small strains."

5. The damping properties of copper crystals do not change with time at room temperature, and are not affected by vibrations of the amplitude employed.

6. The zinc crystals exhibit the phenomenon of recovery at room temperature. Their internal friction is increased by all but the smallest oscillating stresses.

7. The internal friction of zinc crystals depends in such a manner on the angle between the rod axis and the hexagonal axis as to indicate that the rate at which the energy of vibration is dissipated is determined primarily by the resolved shear stress on the slip plane.

8. The resonant frequencies of the crystal rods change as the vibration amplitude is increased in a way that can be correlated with the decrement changes.

9. The internal friction of zinc single crystals is approximately inversely proportional to the frequency.

10. The behavior of these crystals can be explained in terms of the dislocation theory of slip.

ACKNOWLEDGMENT

The writer wishes to thank the New Jersey Zinc Co. for supplying the pure zinc used in these measurements.

REFERENCES

1. T. A. Read: *Phys. Rev.* (1940) **58**, 371.
2. F. C. Nix: *Rev. Sci. Instr.* (1938) **9**, 426.
3. R. F. Miller: *Trans. A.I.M.E.* (1936) **122**, 176.
4. G. I. Taylor: *Proc. Roy. Soc.* (1934) **145-A**, 362.

DISCUSSION

(H. W. Russell presiding)

J. T. NORTON,* Cambridge, Mass.—Dr. Read has done a splendid piece of experimental work in examining these single crystals. It is really the first complete contribution on the internal friction in single crystals, and he has given a logical and practical explanation of one of the possible causes for internal dissipation of energy. The dislocations of Taylor's are well suited to explain some of the aspects of internal energy dissipation. We have all speculated about it more or less, but here seems to be a more or less quantitative confirmation of these ideas. It is quite possible, however, that this is not the whole story.

Clarence Zener has developed what seems to be an adequate explanation of the internal energy dissipation on the basis of thermal currents set up as the crystals in polycrystalline materials are deformed elastically. Strangely enough, the magnitude of the energy dissipation that he found in his experiments is almost identical with that found by Dr. Read.

It seems to me that in the actual case of the energy dissipation in a polycrystalline material both of these phenomena play a part, and it is difficult to see at the moment how much of a

contribution comes from the dislocations and how much comes from something that is in the nature of a nonreversible flow of heat from one part of the specimen to another. I sometimes wonder whether these are not aspects of the same thing. Another possibility that has been considered but that has very little experimental basis in terms of metals is the possibility of some phenomenon related to the primary creep, the reversible part of the creep phenomenon. It would be possible to account for energy dissipation in carrying a crystal through a stress cycle on some such basis. For some of the plastic materials, where the primary creep can be measured accurately and at the same time a damping test can be made, these two seem to check out very nicely; so there is another aspect of the problem. With more experimental work of the kind done by Dr. Read, a much more consistent picture of the whole phenomenon should be obtained.

I think there is some confusion as to the units used to describe internal dissipation of energy, damping capacity, specific damping, and logarithmic decrement. All of those terms are in common use and it would be very helpful if Dr. Read would explain at least the various orders of magnitude involved, and whether they are all more or less the same order of magnitude or quite different.

I also wish he could tell us a little bit more about the actual electrical method of measuring the internal-energy dissipation.

One other question I have is a matter of technique. When Dr. Read makes a composite oscillator of the type he describes, how important is it to have the quartz and the specimen of the same fundamental frequency, and how important is it to have the areas of the two crystals alike? He shows one square and one round. Is it important to have the areas of the cross section exactly alike or does not that make any difference?

W. KAUFMANN,* East Pittsburgh, Pa.—No description is given in the paper of the very striking demonstration given by the author during the oral presentation at the February meeting, of the effect of small amounts of cold-work on the damping of vibrations in an annealed copper bar. Inclusion of such a

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* Westinghouse Research Fellow, Research Laboratory, Westinghouse Elec. and Mfg. Co.

description in the author's closure would be of interest.

The low temperature coefficient of the internal friction indicates that the activation energy for the motion of dislocations must be small (of the order of the average thermal energy, or 600 cal per mol). If the author's interpretation of the "shelf" in Fig. 3 is correct, it should be possible to estimate the size of a dislocation from the activation energy and the magnitude of the stress at which the leveling off of the decrement vs. amplitude curve takes place. Has the author carried out any such analysis?

C. S. SMITH,* Waterbury, Conn.—The author is to be congratulated on a most interesting paper. For the benefit of engineers, it might be pointed out that internal friction is nothing but an easily obtained and extremely sensitive index of the area of a closed stress-strain loop. Many of the effects shown by internal-friction measurements can also be seen on stress-strain curves made with the ordinary instruments of the testing engineer if sufficient care is taken. For example, in a recent paper⁵ describing tests on 70-30 brass, it has been shown that slight overstrain—as little as 0.005 per cent permanent set—will produce measurable curvature of the stress-strain line at stresses far below those at which annealed material ceases to obey Hooke's law. Most copper alloys behave in a like manner, although some precipitation-hardened alloys (beryllium copper) seem to be immune from damage by plastic deformation.

C. S. BARRETT,† Pittsburgh, Pa.—Bruce Chalmers has published measurements on creep that show a phenomenon he calls "micro-creep," which is a reversible creep at low stress levels. He attributes this to the movement of dislocations. The phenomenon and its explanation appear to be closely related to the interesting results of this paper, and I should like to hear Dr. Read's comments on it.

D. L. MARTIN,‡ New Haven, Conn.—The author has clearly demonstrated the application of internal friction as a metallurgical research

tool by his correlation of damping and plasticity of single crystals. The relation of internal friction to the dislocation slip mechanism can be extended to explain several phenomena that have been observed for polycrystalline metals and alloys. By this theory of internal friction solid solution alloys would be expected to possess a lower internal friction than the solvent metals, since the presence of foreign atoms in the parent lattice makes the motion of dislocations more difficult, and, as a result, should decrease the damping capacity. According to Förster and Köster,⁶ alloys do have a lower damping capacity than their components, substantiating this reasoning.

The author states that the copper crystals do not exhibit the recovery phenomenon at room temperature. Köster and Rosenthal⁷ found that the damping of drawn polycrystalline brass decreases with time at room temperature in a manner similar to that shown for zinc in Fig. 8. Table 2 gives the results for a 10 per cent and a 60 per cent drawn brass rod, showing that the heavy reduced material shows the more pronounced drop. This being the case, it would be of interest to know whether an

TABLE 2.—Influence of Time at Room Temperature on Damping of Drawn Brass^a

| Reduction Brass Rods, Per Cent | Time, Hours | | | |
|--------------------------------------|--------------------|-----|-----|-----|
| | 0 | 10 | 20 | 100 |
| | Damping— 10^{-4} | | | |
| 10 | 5.1 | 2.5 | 2.4 | 2.0 |
| 60 | 15.5 | 5.5 | 5.0 | 3.0 |

^a After Köster and Rosenthal.

elongation of the copper crystal would not produce an effect similar to that of the sawed zinc crystal.

An analogous example of recovery at room temperature is shown for pure aluminum (Fig. 17). Förster and Breitfeld,⁸ in determining this time-damping curve, were able to obtain absolute values in 3 or 4 sec. with an accuracy of about 2 per cent. It was thus possible to follow the damping of the pure

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⁵ C. S. Smith: Proportional Limit Tests on Copper Alloys. *Proc. Amer. Soc. Test. Mat.* (1940) 40, 864-884.

† Metals Research Laboratory, Carnegie Institute of Technology.

‡ Hammond Laboratory, Yale University.

⁶ Förster and Köster: *Ztsch. Metallkunde* (1937) 29, 116.

⁷ Köster and Rosenthal: *Ibid.* (1938) 30, 345.

⁸ Förster and Breitfeld: *Ibid.* (1938) 30, 343.

aluminum rod with an initial 6 kg. per sq. mm. load during an increase in the load of 0.25 kg. per sq. mm. (365 lb. per sq. in.). This increase was applied over a time of 45 sec. and resulted

value as an upper limit to the thermal current contribution to the damping.

The two commonest measures of internal friction or damping capacity (these two terms

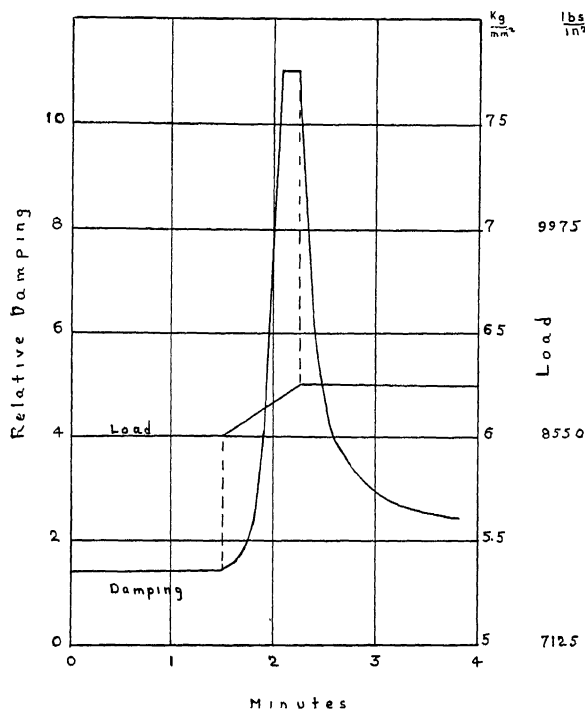


FIG. 17.—DAMPING OF ALUMINUM DURING INCREASING LOAD, AND RECOVERY. (AFTER FÖRSTER AND BREITFELD.)

in a tenfold increase in damping. After the loading, the damping immediately decreased exponentially to a value somewhat higher than the initial one.

T. A. READ (author's reply).—In many cases it is possible to discriminate between the contributions to the damping of a metal that arise from plasticity and from the flow of thermal currents. The latter contribution has been thoroughly investigated by Zener,⁹ as referred to by Professor Norton. The separation is based on the fact that the thermal current damping is *independent of the amplitude of vibration*. Consequently, if measurements are made of the damping over a range of amplitudes, we may take the smallest observed

are synonymous) are the specific damping D and the logarithmic decrement Δ . They are related by

$$D = \frac{\Delta W}{W} = 2\Delta$$

where ΔW is the energy dissipated per cycle in the specimen and W is the maximum potential energy stored in the specimen during the cycle of vibration.

A complete description of the method of measurement will be found in an earlier paper by the author (ref. 1). It is not necessary that the area of the quartz and specimen be the same. On the other hand, the frequencies of the specimen and the quartz must be the same to about 0.5 per cent, as mentioned in the paper, for otherwise there is a contribution to the damping from the adhesive film between the specimen and quartz.

⁹ C. Zener and R. H. Randall: *Trans. A.I.M.E.* (1940) 137, 41.

As mentioned by Dr. Barrett, Chalmers has suggested the movement of dislocations as a mechanism to account for the microcreep he observed in single crystals of tin. There are,

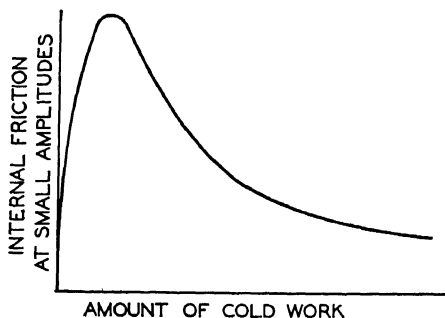


FIG. 18.—SCHEMATIC ILLUSTRATION OF DEPENDENCE OF INTERNAL FRICTION OF COPPER ROD ON AMOUNT OF COLD-WORK IT HAS RECEIVED.

The maximum of the curve corresponds roughly to dropping the annealed rod on a wood surface from a height of several inches.

however, two striking differences between microcreep and the damping of metal single crystals. First, the initial rate of microcreep is proportional to the stress up to 100 grams per sq. mm., whereas over the same stress range the damping increases rapidly with the stress. Note that an inelastic strain rate proportional to the stress should give rise to a decrement independent of the amplitude. Secondly,

Chalmers states that the amount and rate of microcreep is insensitive to slight amounts of cold-work. Internal friction, on the other hand, is affected markedly even by handling the specimen.

The effect of cold-work on the internal friction of copper may be demonstrated easily on a polycrystalline specimen of large grain size, such as a cast rod. If such a specimen is annealed 30 min. at 250°C. and slowly cooled to room temperature, it will have very low damping, as may be shown by suspending it by a thread and tapping it lightly with a mallet. Dropping the specimen on a wooden surface from a height of 3 in. suffices to remove the effect of this annealing completely; it is then "dead soft" and cannot be made to ring at all. Severe cold-work, however, lowers the damping to a value comparable to that after the anneal. This dependence of the internal friction on the amount of cold-work is represented schematically in Fig. 18.

An estimate of the size of a dislocation has been made from internal-friction data, as suggested by Dr. Kauzmann. The value of qAl , the measure of the size of a dislocation used by Dr. Kauzmann¹⁰ obtained in this manner is $1.6 \times 10^4 \text{ \AA}$.³ This agrees in order of magnitude with the values he has obtained from an analysis of creep data.

¹⁰ This volume page 57.

Time and Temperature Effects in the Deformation of Brass Crystals

By H. L. BURGHOFF* AND C. H. MATHEWSON,† MEMBERS A.I.M.E.

(New York Meeting, February 1941)

THE study of the creep of metals under conditions of prolonged loading has received the attention of many investigators for several years and almost innumerable papers have been published on the various aspects of the subject. As it appeared that much could still be learned from a study of single crystals, the present work was carried out to study the effects of temperature and conditions of loading upon the properties and deformation in tension of single crystals of alpha brass containing about 70 per cent copper and 30 per cent zinc. In particular, it was hoped to obtain information from tests below and above the recrystallization temperature of the material, so that properties such as elastic limit, yield point or critical stress, and manner of deformation might be compared for tensile tests at an ordinary loading rate and for prolonged loading.

Accordingly, short-time tensile tests and creep tests were made at room temperature, 300°, 500° and 700°F. The two latter temperatures are above the lowest possible recrystallization temperature of polycrystalline 70-30 brass.

PREVIOUS WORK

Clarke and White¹ have made creep tests of some copper-zinc alloys, including 70-30

From a part of a dissertation presented by H. L. Burghoff to the Faculty of the School of Engineering of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Engineering. Manuscript received at the office of the Institute Nov. 27, 1940. Issued as T.P. 1288 in METALS TECHNOLOGY, February 1941.

* Research Metallurgist, Chase Brass and Copper Co., Inc., Waterbury, Conn.

† Professor of Metallurgy, Yale University, New Haven, Conn.

¹ References are at the end of the paper.

brass, and copper-zinc-tin alloys at temperatures both below and above the recrystallization temperature of the materials considered. Hanson and Wheeler² have studied the flow and fracture of single crystals of aluminum for short-time and prolonged tensile loading over a range of temperature extending from room temperature to 400°F., their experiments being made without consideration of the orientations of the test specimens. Extensive creep and fracture tests on single crystals of lead at room temperature have been made by Betty³ and by Baker, Betty and Moore.⁴ Results of the last-named investigation were published while the present work was in progress. Miller⁵ examined the elastic limit of zinc single crystals at and above room temperature by means of creep tests, while Miller and Milligan⁶ reported the results of tests designed to show the influence of temperature on elastic limit of single crystals of aluminum, silver and zinc.

The behavior of iron crystals under static tensile loading at room temperature was reported by Gensamer and Mehl⁷ while the present investigation was in progress. Their specimens exhibited a well-defined yield point, below which no appreciable creep could be detected. The manner of yielding proved interesting, as the shape of the creep-time curve for the iron crystals differed from the common type of creep curves. Elongation did not begin immediately, or at least was initially very slow. The rate of elongation then increased continuously and finally decreased to zero. This S-shaped type of elongation-time

curve was reproduced at progressively higher loads and was confirmed for several specimens.

PREPARATION OF MATERIALS

The crystals were made by the Bridgman method in the form of rods of $\frac{1}{2}$ -in. diameter and about 9 or 10 in. long. Material for the crystals was high-grade 70-30 brass containing the following maximum amounts of impurities: 0.006 per cent Pb, 0.008 per cent Fe, and 0.002 per cent Ni. The finished crystals contained about 71 per cent Cu.

In preparation for testing, the specimens were carefully machined to a diameter of about 0.450 in. to permit a gauge length of 6 in., annealed for 16 hr. at 1350°F. to reduce coring, and then cleaned or etched in nitric acid solution.

Orientations of specimens before and after testing were determined by Greninger's back-reflection Laue method.⁸ The octahedral plane of maximum shear stress, the active slip plane, was determined by the Taylor and Elam method⁹ and the tangential component of stress along this plane was calculated from Elam's formula:¹⁰

$$S = \frac{P}{A} \sin X \cos \lambda$$

where S = resolved shear stress,

P = applied load,

A = area of cross section of specimen,

X = angle between $\{111\}$ and specimen axis,

λ = angle between $[101]$ and specimen axis.

The theoretical final position of the specimen axis (final orientation) was also determined for comparison with the position actually observed, the calculation being made from Schmid and Boas' formula:¹¹

$$\sin X_1 = \sin X_0 \frac{l_0}{l_1}$$

where X_1 = final angle between slip plane $\{111\}$ and specimen axis,

X_0 = original angle between slip plane $\{111\}$ and specimen axis,

l_0 = original length of specimen = 1

l_1 = final length of specimen = 1 + total elongation.

Knowing the angle between the slip plane and the final position of the specimen axis, and the course of movement of the specimen axis on the stereographic projection according to the Taylor and Elam theory, the theoretical position was readily plotted.

EXPERIMENTAL WORK

Most of the tests concerned with the effect of temperature upon properties of the crystals were performed with the equipment devised by Miller^{5,6} for his work on crystals of zinc, aluminum, and silver. In this equipment the specimen was suspended in a heavy steel frame and connected at the bottom to a balanced 6 to 1 lever. Testing temperatures above room temperature were attained by means of an electrically heated vertical tube furnace which surrounded the test specimen. The temperature was controlled by means of an automatic potentiometer controller.

Loading of the specimen was accomplished by allowing sand to run slowly from a reservoir into a bucket suspended from the longer arm of the 6 to 1 lever. The weight of sand applied was readily measured by means of a Toledo scale, which supported the sand reservoir and was graduated to read to 0.1 lb. The rate of loading was approximately constant at about 7 lb. per minute, and readings of load, extension, and specimen temperature were taken for increments of 12 or 24 lb. as desired. At critical periods in some of the tensile tests, readings were taken at more frequent intervals.

Extension of the specimen was measured by means of a microscope extensometer with which it was possible to make readings to an accuracy of $\pm 6.6 \times 10^{-6}$ in. per inch. Errors of reading due to thermal expansion

and contraction of the sleeve supporting the microscopes of the extensometer were eliminated by checking readings for the distance between the two by a standard quartz rod. Inasmuch as specimen temperature could not be maintained at 1°F. was definitely significant, for it meant a difference of approximately two divisions of the filar micrometer eyepiece. Tests made at room temperature with this equipment were without benefit of temperature control, but specimen temperature was

TABLE I.—*Data and Test Results for Crystals Tested*

| Specimen No. | X_0 ($P \wedge \{111\}$), Deg. | λ_0 ($P \wedge \{101\}$), Deg. | $\sin X \cos \lambda_0$ | Young's Modulus of Elasticity, Grams per Sq. Mm. | Critical Max. Resolved Shear Stress, Grams per Sq. Cm. | Total Extension, Per Cent | Resolved Creep Stress, Grams per Sq. Mm. |
|------------------------------|--|--|-------------------------|--|--|---------------------------------|--|
| Room Temperature (70°–80°F.) | | | | | | | |
| 35-1 | 43½ | 49 | 0.451 | | 1,465 | 12.5 | |
| 14-2 ^a | 33 | 43 | 0.397 | | 1,440 | 7 | |
| 31-1 ^a | 53 | 58½ | 0.416 | | 1,400 | 7 | |
| 12-1 ^a | 28 | 30 | 0.406 | | 1,370 | 38 | |
| 29-1 ^a | 47 | 48 | 0.489 | 14.1 × 10 ⁶ | 1,395 | 13 | |
| 8-4 | 32½ | 32½ | 0.452 | 6.8 × 10 ⁶ | 1,300 | 0.5 | |
| 12-3 | 39 | 39½ | 0.485 | 8.5 × 10 ⁶ | | | 750; 900; 1000; 1100 |
| 32-2 | 45½ | 46 | 0.496 | | | 12.7 | 1200; 1300 |
| 28-1 | 41½ | 43 | 0.484 | | | 5.0 | 1100 |
| 300°F. | | | | | | | |
| 8-3 | 23½ | 35 | 0.327 | 12.7 × 10 ⁶ | 1,035 | 0.29 | |
| 11-3 | 30½ | 31 | 0.434 | 7.7 × 10 ⁶ | 1,220 | 3.0 | |
| 30-2 | 41½ | 43 | 0.484 | | | 10 | 800; 1000; 1100; |
| | | | | | | | 1200 |
| 30-3 | 52 | 56½ | 0.435 | 12.7 × 10 ⁶ | 1,100 | 7.3 | 1000; 1100 |
| 500°F. | | | | | | | |
| 14-1 | 39½ | 46 | 0.441 | 18.5 × 10 ⁶ | 1,150 | 9 | |
| 11-4 | 42½ | 42½ | 0.497 | 5.1 × 10 ⁶ | 1,140 | 6 | |
| 30-1 | 35½ | 42 | 0.430 | 14.9 × 10 ⁶ | | 4 | 300; 450; 600; 800; |
| | | | | | | | 1000; 1100 |
| 29-2 | 39½ | 43½ | 0.460 | 3.1 × 10 ⁶ | | 11 | 1000; 1100 |
| 700°F. | | | | | | | |
| 1 | 37 | 38 | 0.474 | 9.4 × 10 ⁶ | 1,290 | 4 | |
| 12-4 | 46 | 42 | 0.534 | 5.6 × 10 ⁶ | 1,420 | 13 | |
| 7-4 | 41½ | 47 | 0.451 | | | 0.22 | 200; 300; 450 |
| 31-3 | 38½ | 41½ | 0.466 | 4.0 × 10 ⁶ | | 0.72 | 600 |

^a See reference 13.

absolutely constant value during any test, it was essential to correct observed readings of extension for variations in temperature. Specimen temperature therefore was determined at each step in a test. Instantaneous specimen temperatures were read to 1°F. and corrections to be applied to the observed extension were calculated using instantaneous coefficients of expansion derived from National Bureau of Standards data.¹² A change in temperature of only

recorded with each reading of extension as usual. For all tests above room temperature auxiliary thermocouples were wired securely to the specimen near each reference mark for the purpose of adjusting furnace heating to obtain uniform temperature distribution in the specimen.

A number of tensile tests were made at room temperature with a hydraulic tensile testing machine. A stress-strain recorder drew the load-elongation curve up to 0.5

per cent elongation in the 2-in. gauge length required with this apparatus.

Tests with the weight and lever loading device were made at room temperature

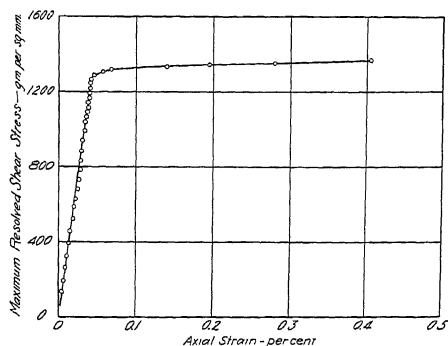


FIG. 1.—RESOLVED STRESS-STRAIN CURVE FOR SPECIMEN 8-4 IN TENSION AT ROOM TEMPERATURE.

(70° to 80°F.), 300°, 500° and 700°F., and included slow tensile tests, in which the specimens were extended only until appreciable plastic deformation occurred, and prolonged tests at constant load for each temperature.

DISCUSSION OF RESULTS

Tests at Room Temperature

Data concerning the specimens tested at room temperature, as well as some test results, are shown in Table 1.

The several specimens subjected to short-time tests in the tensile testing machine showed a definite yield point; i.e., a slight decrease in stress as the first plastic deformation began. The extent of stress decrease in this region is illustrated by the behavior of specimen No. 35-1. The stress-strain curve for this specimen was linear until yielding occurred at a maximum resolved stress of 1465 grams per square millimeter. There was a distinct yield point and the resolved stress decreased to 1410 grams per sq. mm. during the first plastic extension. This decrease was soon followed by an increase in load as the specimen strain-hardened. The yield points or critical maxi-

mum resolved shear stresses obtained in these short-time tests are in agreement with the results obtained for similar brass crystals by Sachs and his co-workers.^{14,15}

Those specimens loaded by the weight-and-lever method naturally could show no decrease in stress as the specimens yielded. A stress-strain curve typical of this means of loading is illustrated by that for specimen No. 8-4 in Fig. 1. Stress is proportional to strain substantially to the critical resolved shear stress, as with other specimens tested. The departure from this first slope of the stress-strain curve is very great as plastic extension begins.

Creep tests or tests under prolonged loading conditions were made with three specimens. Specimen No. 12-3 was successively loaded at 750, 900, and 1000 grams per sq. mm. for periods of 505, 335, and 335 hr., respectively. No creep could be observed in these conditions and, indeed,

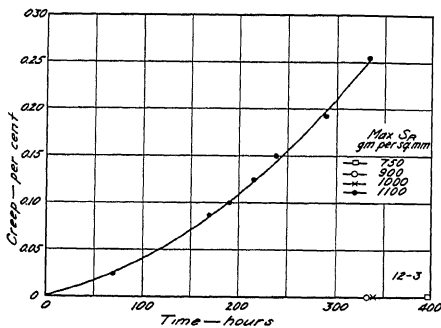


FIG. 2.—CREEP-TIME RELATIONS FOR SPECIMEN 12-3 AT ROOM TEMPERATURE; MAXIMUM RESOLVED SHEAR STRESS INCREASED SUCCESSIVELY AS INDICATED.

the stress-strain curve from zero stress to 1000 grams per sq. mm. was definitely a straight line. The stress-strain curve was still linear when the load was increased to 1100 grams per sq. mm. resolved shear stress, but creep then occurred at an increasing rate for a period of two weeks, at which time the test was terminated. The course of the creep-time curve is shown in Fig. 2; the total creep extension during this period was 0.26 per cent.

This test appeared to show the existence of a definite creep limit between 1000 and 1100 grams per sq. mm. resolved stress, below which no creep occurred, at least within the limit of accuracy of the test. The critical stress, elastic limit, or yield point, however named, is thus definitely lower for prolonged than for brief loading. This test gave the first indication that the early part of the creep process in these single crystals of brass takes place at an increasing rate, a phenomenon that was verified with other specimens.

Specimen No. 32-2 was loaded to 1200 grams per sq. mm. resolved stress, and stress was proportional to strain over this range. It was intended that creep observations should be made at this stress and the load was accordingly held constant. No discernible creep took place in 20 min. However, in the ensuing 22-hr. period, during which no readings could be taken, the specimen had elongated practically 10 per cent and was still deforming or creeping, but at a very low rate, after that time. The deformation soon stopped completely, as no further creep was detected in the period from 50 to 137 hr. total time. The extension must have started at an increasing rate, soon attaining a maximum rate and thereafter decreasing to a lower rate as the specimen strain-hardened.

The load was then increased to 1300 grams per sq. mm. resolved stress; extension, for which complete data were obtained, began again immediately. The creep occurred at an initially increasing rate (Fig. 3) and attained a maximum velocity within an hour. This rate was maintained for a short time but thereafter decreased rapidly, so that the creep curve was virtually flat in 5 or 6 hr. The specimen had elongated 2.8 per cent additionally during this period and crept only 0.02 per cent further from this point through 24 hr. elapsed time at this stress. No measurable creep occurred from 24 to 193 hr. The results attained on this specimen were similar

in character to the results obtained by Mehl and Gensamer in creep tests of iron crystals.

Specimen No. 28-1 was also made the

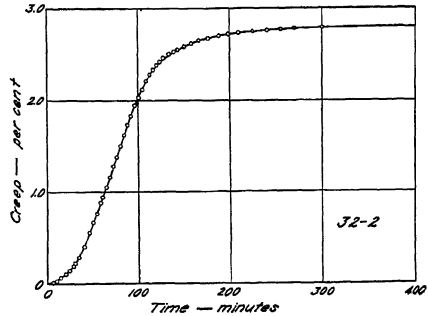


FIG. 3.—CREEP-TIME CURVE FOR SPECIMEN 32-2 AT ROOM TEMPERATURE; MAXIMUM RESOLVED SHEAR STRESS = 1300 GM./SQ. MM. PREVIOUSLY EXTENDED 10 PER CENT AT RESOLVED STRESS OF 1200 GM./SQ. MM.

subject of a creep test, maximum resolved shear stress in this case being 1100 grams per sq. mm. The stress-strain curve obtained in loading was linear to this stress. As shown in Fig. 4, creep occurred at an initially increasing rate, attaining a maximum velocity between 400 and 700 hr. elapsed time, during which the specimen extended from 0.5 to 4 per cent. The creep rate decreased markedly beyond 700 hr., becoming extremely low after 1200 hr. The test was finally terminated after about 1600 hr., at which time the total extension was 5.0 per cent.

The load was then released to 74 grams per sq. mm. resolved stress, which low value was desirable in maintaining proper alignment for observation so that a study of creep recovery could be made. The specimen immediately contracted 0.034 per cent, which corresponded exactly to the extension of the specimen when loaded from 74 to 1100 grams per sq. mm. No further contraction or creep recovery was observed over a period of 92 hours.

During the course of the creep test on this specimen, an effort was made to count the number of slip lines or bands as the

test proceeded. This could be done roughly in the initial stages but it soon became impossible to keep any reasonable record of the markings. The slip bands increased in

velocity, but to a variation in the number of operating slip planes.

As explanation for this, it is visualized that slip first occurs on a few planes and

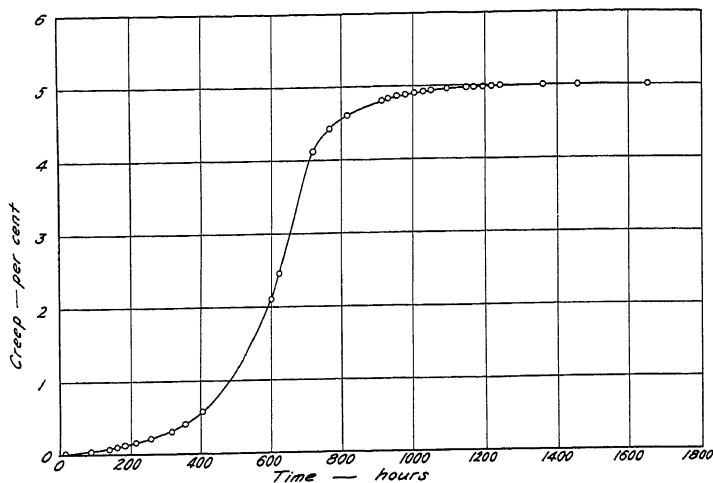


FIG. 4.—CREEP-TIME CURVE FOR SPECIMEN 28-1 AT ROOM TEMPERATURE; MAXIMUM RESOLVED SHEAR STRESS = 1100 GM./SQ. MM.

number at an increasing rate (Fig. 5) until about 75 bands had been counted. Thereafter slip markings became so numerous that any attempt to count them was futile.

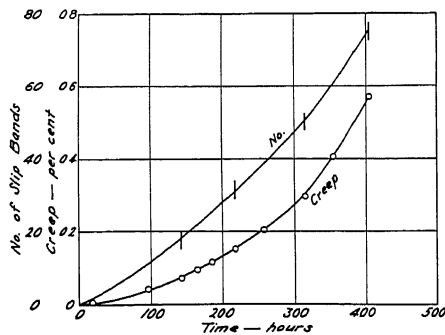


FIG. 5.—RELATIONSHIPS AMONG AMOUNT OF CREEP, NUMBER OF VISIBLE SLIP BANDS, AND TIME DURING THE INITIAL STAGE OF CREEP OF SPECIMEN 28-1.

It appeared that the number of visible slip markings increased directly as extension increased and that the variation in creep rate was due, not to a change in slip

then takes place on additional planes through a migration of stress concentrations. The initially increasing rate of extension is viewed as resulting from the great availability of unhardened potential slip planes with stress concentrations serving to accelerate the number of participating slip planes during this time. As the metal begins to strain-harden and the number of available unhardened slip planes decreases, the over-all rate of extension naturally decreases and may approach zero. This explanation may be further amplified by considering that, for a given load, slip along a participating plane takes place at substantially constant rate with no variation in such individual slip velocity being required to explain apparent creep rates of a specimen. However, it may well be that such slip velocity along a plane is a function of the applied stress, or additionally, the shear or displacement along the plane may be a function of the stress.

Such an explanation is not made in terms of any particular mechanism of slip and contains an assumption that all of the slip bands observed may be operating at the same time. One of the authors has proposed (private distribution, typescript) a form of slip in which moments of reversed shearing force derived from a rearrangement of the atoms at the yield point oppose smaller moments of externally applied elastic shearing force, to give slip with a residue of stress in strained spacings at and near the site of slip. Strain-hardening from this point of view is residual stress developed by slip. Slow recovery from this condition by equalization of internal strain through the lattice would decrease the additional stress required to produce further slip and remove preexisting restrictions as to the site of slip. Under constant application of a fixed load as in these tests the effect would seem to be not unlike that of decreasing friction at a sliding contact, thus permitting a quicker response to the load. Recovery, however visualized, is known to be effective during a slow straining process. If complete, no strain-hardening occurs and if incomplete the normal amount of strain-hardening is reduced. The stress-strain curve plotted in Fig. 1 reveals inconsequential strain-hardening in the early stage of deformation conducted at a loading rate of approximately 30 grams per sq. mm. per minute.

All specimens tested at room temperature, whether in the short or prolonged tests, showed slip markings due to plastic extension. In every case it was found that these markings corresponded to the $\{111\}$ plane of maximum resolved shear stress. For specimens that suffered appreciable extension, the change in orientation was as prescribed by movement along a $\{111\}$ plane in $[101]$ direction.

Tests at 300°F.

Both short and long-time tests were made at 300°F., four specimens in all being investigated at this temperature. Data con-

cerning the specimens used and some test results obtained are summarized in Table 1. Tests at this temperature indicated that the critical shear stress, the stress at which

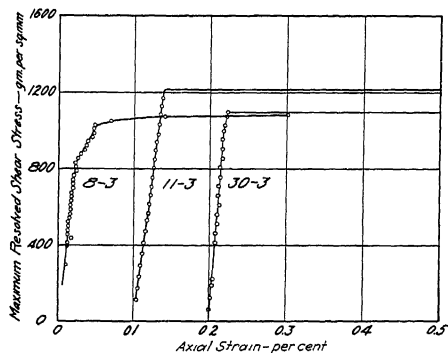


FIG. 6.—RESOLVED STRESS-STRAIN CURVES FOR SPECIMENS 8-3, 11-3, AND 30-3 IN TENSION AT 300°F. (CURVES OFFSET FROM ORIGIN FOR CLEARNESS.)

substantial yielding occurs, is somewhat lower in short-time tests than the values obtained at room temperature. Furthermore, the yielding was much more abrupt and was difficult if not impossible to follow with the available measuring means during the first part of the plastic extension. As shown in Fig. 6, the stress-strain curves for these short-time tests were substantially linear up to the point of actual plastic flow.

Specimen No. 30-2 was subjected successively to stresses of 800, 1000, and 1100 grams per sq. mm. for periods of 95, 70, and 95 hr., respectively, during which no creep was observed. When this stress was increased to 1200 grams per sq. mm., not more than 0.0013 per cent extension or creep occurred in the first $3\frac{1}{2}$ hr. at the higher stress, but before 28 hr. had elapsed (during which time no intermediate readings could be taken) the specimen had extended 10 per cent. It must be assumed that such extension took place with initially accelerating and later decelerating rate. No further creep was observed after this time up to 168 hr., when the test was terminated.

Specimen 30-3 was held for 96 hr. at 1000 gram per sq. mm. resolved stress and no

apparent creep occurred. When the stress was increased to 1100 grams per sq. mm. no apparent plastic extension occurred, for a minute or so and then a barely perceptible

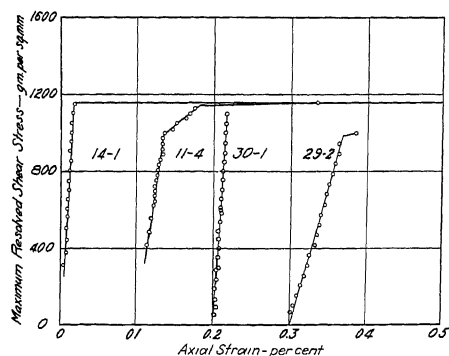


FIG. 7.—RESOLVED STRESS-STRAIN CURVES FOR SPECIMENS 14-1, 11-4, 30-1, AND 29-2 IN TENSION AT 500°F.

movement or deformation of the specimen was noticed, which increased in rate, then decreased, and stopped. The extension, which was nearly 7.5 per cent, took place in an interval of not more than 2 min. This test was continued for a period of 163 hr., during which time no further extension could be observed. There was again indicated a time-elongation curve of shape similar to those obtained at room temperature with rate first increasing, later decreasing, and finally approaching zero as hardening occurred.

Slip markings were visible on all specimens tested at this temperature and corresponded to the {111} plane of maximum shear stress. Orientation changes were as usually prescribed in terms of slip and rotation.

Tests at 500°F.

Both short-time and long-time tests were run at 500°F., four specimens being thus tested. Specimen data and some test results for this group are also given in Table I.

The short-time tests showed, as at 300°F., that yielding, once started, is much

more abrupt than at room temperature and continues for a considerable extension without increase in load. The critical resolved shear stress was found to be only slightly less than at room temperature. The tests made for conditions of prolonged loading indicated the existence of a creep limit essentially the same as at room temperature; i.e., approximately 1000 grams per sq. mm. maximum resolved shear stress, in spite of a temperature well above the lowest possible recrystallization temperature of polycrystalline metal of the same composition.

Specimen No. 30-1 was successively loaded to 300, 400, 600, 800, and 1000 grams per sq. mm. resolved stress for periods of 165, 409, 166, 168, and 72 hr., respectively. At none of these stresses was creep observed. The stress-strain data obtained in the interrupted loading of the specimen over this long period of time show (Fig. 7) a substantially straight line or proportional range up to 1000 grams per sq. mm. and also up to 1100 grams per sq. mm., which was the highest and final stress used. When the load was increased to this last value, no visible extension of the specimen occurred during at least 6 hr. However, after that time and in less than 48 hr., the specimen had elongated 4 per cent and then the extension had presumably been stopped because the loading lever came to rest against the supporting structure. It would appear, therefore, that the first extension must have taken place at an increasing rate.

It was evident that within the limits of the test there was a creep limit for this specimen between 1000 and 1100 grams per sq. mm. resolved shear stress.

Stress-strain data were obtained for specimen No. 29-2 up to 1000 grams per sq. mm. resolved stress. The stress-strain curve was linear (Fig. 7) up to 935 grams per sq. mm., but deviated slightly in the last loading increment. The specimen was loaded immediately above the short-time propor-

tional limit for the prolonged test that was then started. There was no visible creep for $1\frac{1}{2}$ hr. and only a possible slight indication of creep (0.00135 per cent) after 2 hr. However, in 22 hr. the creep mounted to 0.0155 per cent, after which the rate decreased and became almost negligible after 168 hr., the total time at this stress. The now familiar creep curve with initially increasing and later decreasing rate therefore describes the deformation at this stress.

Maximum resolved shear stress was then increased to 1100 grams per sq. mm. and no visible creep occurred for almost 2 hr. Then while a reading for the 2-hr. interval was about to be taken the specimen began to yield or slip visibly and uniformly for not longer than 1 min., when apparently it stopped. It was established that the specimen had elongated 2.5 per cent during this interval. It was obvious that the sudden deformation had started at an increasing rate and later had slowed down. The same load was maintained for a total time of 263 hr. after the sudden 2.5 per cent extension and it was found that there was a rapid although small flow to 0.023 per cent additional extension in 3 hr. after the sudden yielding. After this, creep rate was much less and tended to decrease with increasing time.

Load was successively increased to 1150 and 1230 grams per sq. mm. for periods of 239 and 167 hr. Creep occurred at a decreasing rate for both stresses and both rates were little greater than the final rate at 1100 grams per square millimeter.

When the load was finally increased to 1435 grams per sq. mm. resolved stress, the specimen immediately yielded and its movement was stopped only when the lever came to rest on the supporting frame.

Slip markings were observed on all specimens tested at this temperature. These markings again corresponded to the {111} plane of maximum resolved shear stress and orientation changes were of the normal type.

Tests at 700°F.

The tests at 700°F. yielded results among the most interesting of the entire investigation, as it was more readily possible to

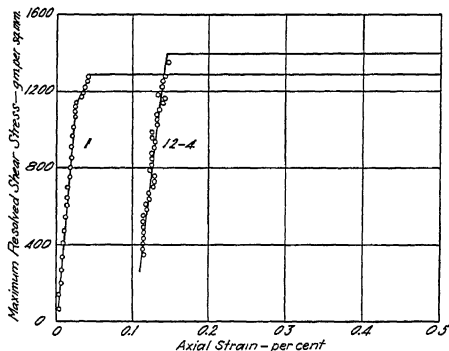


FIG. 8.—RESOLVED STRESS-STRAIN CURVES FOR SPECIMENS 1 AND 12-4 IN TENSION AT 700°F.

follow the course of creep than at 300° or 500°F. Moreover, greater differences in behavior were found between short and prolonged tests. Data for the test specimens are given in Table 1.

Stress-strain curves obtained for the ordinary rate of loading of specimens 1 and 12-4 are shown in Fig. 8. The curves show abrupt and considerable yielding at maximum resolved shear stresses of 1290 and 1420 grams per sq. mm., respectively, values that are approximately the same as those obtained in the previously described room-temperature tests.

Slip markings were visible on the surface of these specimens in spite of oxidation, and were found to correspond to the proper slip plane as predicted for room-temperature deformation.

Creep data were obtained for specimen No. 7-4 for maximum resolved shear stresses of 200, 300, and 450 grams per sq. mm., respectively. In spite of being far below the critical stress or yield point of the short-time test, each of these stresses produced distinct creep at ever increasing rates (Fig. 9). The testing of this specimen was terminated when the total creep for the

entire test was 0.22 per cent. The deformation being small and the surface oxidized, no slip markings were visible.

It seems logical to assume that creep

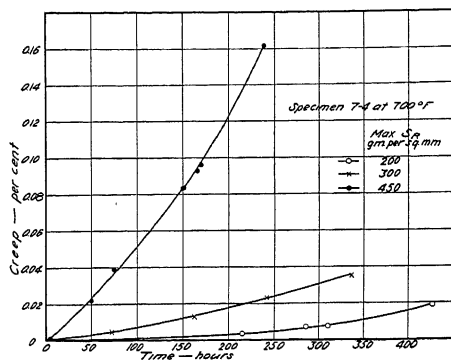


FIG. 9.—CREEP-TIME CURVES FOR SPECIMEN 7-4 AT 700°F.; MAXIMUM RESOLVED SHEAR STRESSES INCREASED SUCCESSIVELY AS INDICATED.

would have taken place at any stress at this and higher temperatures. Furthermore, it would seem probable that higher stresses in the vicinity of the knee of the stress-strain

amounted to 0.125 per cent. The curve thereafter became concave to the time axis as creep rate decreased.

No slip markings were visible on the blackened surface of the specimen, but it was found that the cross section had changed definitely, although only very slightly, from a circular to an elliptical shape, which made possible the location by X-ray means of the zone containing the operating slip plane. This zone proved to contain the predicted $\{111\}$ plane of maximum resolved shear stress. There was again no indication of any new or different manner of deformation.

SUMMARY

As tested by the usual tension-testing procedure, at room temperature, single crystals of 71-29 brass show a small but definite drop in load as plastic deformation first begins, indicating the existence of a yield point as in iron crystals. Critical maximum resolved shear stress in slow tensile

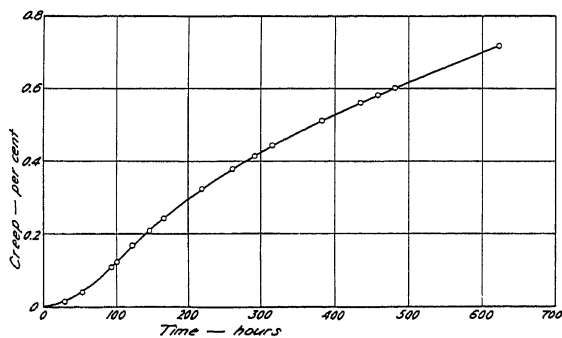


FIG. 10.—CREEP-TIME CURVE FOR SPECIMEN 31-3 AT 700°F.; MAXIMUM RESOLVED SHEAR STRESS = 600 GM./SQ. MM.

curve would give results similar to those for specimen No. 29-2 at 500°F., but with greater creep and less hardening effect.

Specimen No. 31-3 was subjected to prolonged loading equal to a maximum resolved shear stress of 600 grams per sq. mm. for 625 hr. The course of the creep curve is shown in Fig. 10. Creep rate increased during the first 100 hr., at which time extension

tests ranged from about 1300 to 1465 grams per sq. mm. at room temperature, agreeing well with test results of previous investigations, and was not substantially changed at 300°, 500°, and 700°F. The yielding or first plastic deformation in such tests became more abrupt and rate of the yielding became more rapid as the test temperature increased.

Creep tests or tests under conditions of prolonged, constant load revealed the existence of a true elastic limit or creep limit, at least within the sensitivity of the tests, below which no plastic deformation was observed throughout periods as high as several hundred hours. This limit corresponded to a maximum resolved shear stress of about 1000 to 1100 grams per sq. mm., and was substantially unchanged from room temperature to 500°F. At 700°F., appreciable creep occurred for resolved stresses as low as 200 grams per sq. mm. and it seemed probable that creep would take place at any stress at this or higher temperatures.

The initial plastic deformation in the creep tests at all temperatures took place at an increasing rate, the rate later decreasing and, for the lower temperatures, apparently approaching zero. Evidence was found to show that the amount of creep was directly proportional to the number of slip bands defining planes that must have operated either simultaneously or in succession during the process. Alternative explanations of this structural effect are possible.

Observation of dimensional changes and slip markings correlated with X-ray analysis indicated that the manner of deformation was the same for all tests in the investigation; that is, by slip upon {111} planes in [101] directions with orientation changes as classically predicted.

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DISCUSSION

(J. J. Kanter presiding)

R. M. BRICK* New Haven, Conn.—As everyone knows, who has worked with this type of cast crystal, the specimens were not true single crystals. Laue reflection pictures of the crystals usually show multiple spots. The angular difference between the different dendritic axes varies from one crystal to another. I should like to ask the authors if they noticed, studying all these crystals with varying degrees of imperfections, whether there was any difference in the critical resolved shear stress at a given load and temperature between a rather imperfect crystal and one less imperfect.

A second point relates to the author's remarks in regard to observations of slip markings on the surface of the crystals. These are interesting, particularly so in regard to claims that creep is not essentially a slip mechanism but a viscous flow mechanism. The slowing up in the creep rate and ultimate stoppage is attributed to possible exhaustion of unstrain-hardened slip planes. I should like to mention some tensile deformation experiments on single crystals that Dr. Burghoff made up but did not use, and left at the laboratory.

At a 2 per cent extension (under ordinary loading rates) which in some of his experiments might represent the maximum extension obtained before creep stopped, numerous slip markings would be visible to the naked eye. If a flat section of the specimen had been polished before the extension occurred, and one of these slip lines was examined at a high magnification of 1000 diameters, it would be found to be made up of a tremendous number of lines. We have made tests where the crystal was stressed to a very slight extension of perhaps 0.1 per cent, at which point a few markings first appeared. In one specific "macro" line, five or six of these slip markings would be visible at 1000 diameters. On continued loading of the crystal, the number of these markings increased as Dr. Burghoff indi-

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cated, but, also, at any one single marking where previously there were five or six this might increase up to 20, 40, or 50; within one single location or what would appear to be one line to the naked eye. At extensions approaching the maximum mentioned by the authors, there were still large areas of apparently completely undisturbed metal, and it seems rather incredible that there is not a very large number of undisturbed planes still available for slip.

M. GENSAMER,* Pittsburgh, Pa.—In our work to which Dr. Burghoff referred, we observed an interesting and puzzling thing. When we put on the low loads, there was no creep, of course; when we put on a high enough load, we obtained the kind of creep that Dr. Burghoff described. With a little bit more load, nothing happened. We might make another slight increase in load with no creep. Finally, with a sufficient additional load, creep would be observed. This process could be repeated after each creep observation; we could put a little more load on and not get any more creep, at least not in the time that we could afford to wait. I should like to know whether Dr. Burghoff and Dr. Mathewson have observed a similar effect.

In connection with Dr. Brick's remarks, is not this kind of behavior to be expected when the materials are not really homogeneous? After all, it is expecting a great deal to suppose that every part of a crystal will have the same yield point, the same creep limit.

B. B. BETTY,† Huntington, W. Va.—I have observed some of the things mentioned, in my work on lead. I think spacing of the slip lines, rather uniform spacing in the course of deformation, with partially strained material in between, must be accounted for on the basis of the observations of more detailed and intensive studies that have been made on aluminum single crystals in the National Physical Laboratory, from which it must be concluded that the strain-hardening proceeded at right angles to the plane of slip as well as in the direction of plane of slip. Undoubtedly some of these phenomena are due to the involvement of a larger number of planes as

the degree of work-hardening is intensified. A convenient assumption to make here is that the intensity of work-hardness decreases with increasing distance from the plane in which slip has occurred.

I am interested to see this S-curve, since I have observed something of that kind in polycrystalline specimens for which I have not heretofore had an adequate explanation.

H. L. BURGHOFF (author's reply).—As Dr. Brick says, the crystals were imperfect, as shown by the character of the spots of Laue reflection pictures, and there were real differences in critical resolved shear stresses for given loading conditions. Although no critical study of this situation was made, there was no apparent relation between crystal imperfection and critical stress.

With regard to his second point, it is realized that the unaided eye cannot see the detail of slip markings made evident by a microscope. However, it was felt that the reporting of the occurrence of the slip markings in the particular test cited was interesting and of speculative value.

Referring back to Figs. 4 and 5, the slip bands that were counted were, of course, only the first ones. They increased so rapidly after 400 hr., being distributed over the entire gauge length, that it was no longer feasible to count them. The mechanism of hardening is naturally involved in these considerations, and I think that the theory that Dr. Mathewson is now propounding may lead to some light on the spacing of slip bands and the appearance of subsequent ones. Mr. Betty's remarks are interesting in that they also include consideration of the hardening process.

Dr. Gensamer asked if we had observed any effect due to application of additional load after the original yielding. This is illustrated in the paper for specimen No. 29-2, which was tested at 500°. Considerable yielding was obtained on application of a certain stress. When two or three higher stresses were applied, the specimen still crept, of course, but still at decreasing rates not greatly different from that for the first lower stress. When a still higher load was finally applied, a sudden yielding was experienced, and the specimen elongated as far as the equipment would permit.

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Flow of Solid Metals from the Standpoint of the Chemical-rate Theory

BY WALTER KAUFMANN*

(New York Meeting, February 1941)

ALL viscous or plastic flow of incompressible matter is the result of shear strain; the changing shape of any body that is being plastically deformed can be completely described in terms of the shear strain occurring at each point in the body.[†] Furthermore, the relative amounts of shear strain occurring in different parts of a body under stress depend upon the relative rates of shear strain at those different points, so that if the dependence of the shear rate of any material on the temperature, shear stress, previous history, etc., were understood, the principles of plastic deformation would be known, and we could calculate how a body made of a given material, having a given shape, and subject to a specified system of forces, would change its shape with time. It may be said, then, that the problem of plasticity resolves itself into, first, the problem of the rates of pure shear processes, and second, the application of what is known about pure shear to actual cases. It is the purpose of this work to investigate the former problem—i.e., the dependence of shear rates on temperature, stress, etc.—from the standpoint of recent developments in the field of

chemical-rate theory and with particular reference to the phenomena occurring in the creep of metals and in the plastic flow of crystalline solids in general. It is left for the mechanical engineer, and perhaps the expert in hydrodynamics, to deal with the problem of applications.¹

RESOLUTION OF MACROSCOPIC SHEAR INTO MICROSCOPIC MOVEMENTS; RESEMBLANCE TO CHEMICAL REACTIONS

Just as any large body is made up of many small units, or atoms, so macroscopically observable shear is the result of many microscopic unit shear processes; just as the understanding of the behavior of large bodies demands the understanding of the atoms of which it is made, so the understanding of macroscopic shear demands the understanding of these fundamental unit processes. The study of shear from this "atomistic" point of view has made considerable progress. There has been fairly complete understanding of shear processes in gases for a long time, at least for non-turbulent flow, as a chapter on gaseous viscosity in any text on the kinetic theory of gases will prove. In recent years Andrade² and Eyring³ have presented important theories for the flow of liquids and amorphous solids. Becker,⁴ Orowan,⁵ Taylor,⁶ Burgers,⁷ and Kanter⁸ have considered the plastic flow of crystalline solids from this

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[†] Thus, a plate undergoing deformation as in Fig. 1 may be regarded as made up of a large number of tiny squares, and the change in the shape of the plate is the result of the changed shapes of the squares, which in turn are describable as pure shear strains.

¹ References are at the end of the paper.

point of view, and have derived formulas for the correlation of shear with various other properties of the flowing matter, while Polanyi, Schmidt, Smekal, and many

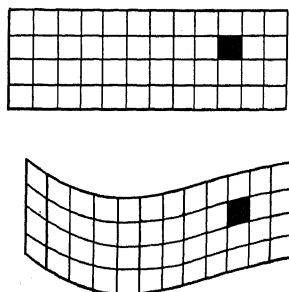


FIG. 1.—PLASTIC DEFORMATION ARISING FROM PURE SHEAR.

others have constantly striven to interpret the results of their work on the deformation of crystalline material in terms of the molecular process occurring in shear.

The point of view that has been adopted in the present investigation of the shear of crystalline solids is that of Eyring, whose general theory of shear rates,⁸ based upon his statistical mechanical equation for rate processes is admirably suited to this problem.⁹ Since, however, this approach was developed with a view to its use in the study of the rates of chemical reactions, the concepts it involves are those most familiar to the chemist, while, on the other hand, the flow of crystalline solids has been of interest chiefly to the engineer and physicist, who are less familiar with these attitudes of the chemist. Therefore, it seems desirable to review here at some length the notions behind the rate equation of Eyring and its application to the general problem of shear rates, and only then to apply it to the specific problem of shear rates in crystals. Before doing this, however, it will be profitable to introduce a few simple notions that will serve to make clear just what features of the problem are similar to those characteristic of chemical reactions.

In what follows, use will be made of the concept of *units of flow*; these are the

structures in a body whose motions past one another make up the unit shear process mentioned above. In a liquid such as water the units of flow are believed to be single

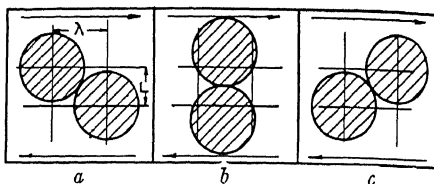


FIG. 2.—MOLECULAR SHEAR PROCESS IN ORDINARY LIQUIDS.

molecules, and the unit process is the passage of single molecules past one another in some such manner as is illustrated in Fig. 2. Here the motion of the molecules through the stages *a*, *b*, *c* has resulted in a shear strain of λ/L in the direction indicated by the solid arrows, while the rate of shear is equal to the shear resulting from each jump times the number of jumps occurring in unit time. Clearly we can in general say that

$$\text{shear rate} = s = \frac{\lambda}{L} \nu \quad [1]$$

where λ is the average distance in the shear direction moved by units of flow past one another in one jump, L is the average distance between layers of units of flow, and ν is the net number of jumps per second made by the unit of flow in the shear direction.

If we can understand how the quantities λ , L , and ν depend on the shear force, the temperature, etc., we shall have as complete an understanding of the phenomenon of shear as will be required for application by the engineer to problems of plastic flow in general.

In solids and liquids, to which the viewpoint of equation 1 is particularly well suited, the distance moved by units of flow and the distance between layers of units of flow are expected to be fixed chiefly by the lattice dimensions of the flowing materials.

The dependence of these on the shear force, temperature, cold-working, and other factors, would certainly not be sufficient alone to account for the very large changes in shear rates that such factors are known to be capable of causing. This makes impera-

exponential dependence of the rate of most chemical reaction on the temperature as follows:

$$\text{rate} = Ce^{\Delta H^*/RT} \quad [2]$$

where ΔH^* is the activation energy re-

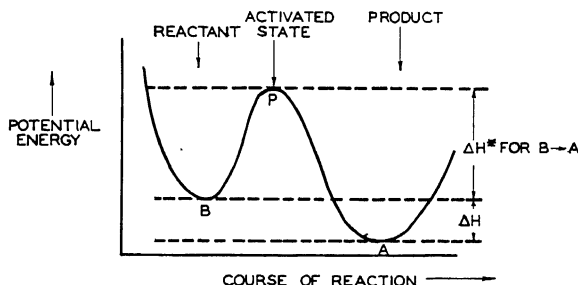


FIG. 3.—TYPICAL POTENTIAL-ENERGY CURVE FOR REACTION $B \rightarrow A$, INVOLVING AN ACTIVATION ENERGY.

tive the thorough understanding of the term involving the rate at which units of flow pass one another, since this term probably contains the greater part of the sensitivity of shear rates to the external conditions.

It is very likely that in order for units of flow to be able to pass one another, especially in solids, a considerable amount of energy is required. (Thus, in Fig. 2*b*, if the surrounding molecules were shown, it would be apparent that there is a great deal of squeezing of the molecules against one another.) This energy may be considerably greater than the ordinary thermal energy of the molecules, so that in order for shear to occur between two units of flow, these must be *activated*. The number of passages of units of flow per second, therefore, is very greatly reduced, since only relatively few of them possess much more than the average thermal energy.

This is exactly the situation that faces the chemist when he seeks to understand the rates at which substances react. Here, too, the reacting molecule or molecules must be activated before the reaction can proceed. As is well known, this requirement of an activation energy gives rise to an

quired by the reacting molecules before they can react, R is the gas constant ($= 1.987$ cal. per mol per degree centigrade), T is the absolute temperature and C is a constant independent of the temperature. It will be found very helpful to represent the course of a reaction by an "energy map"; a typical, simplified one is shown in Fig. 3. The ordinate of such a plot represents the potential energy at any point along an abscissa (here given as "course of reaction") which usually involves one or more interatomic distances. Then if the reaction in question is $B \rightarrow A$, the ΔH^* of Eq. 2 is the same as that shown in Fig. 3, while if the reaction is $A \rightarrow B$, the ΔH^* of Eq. 2 is $\Delta H^* + \Delta H$ in Fig. 3, ΔH being the *heat of the reaction*.

Apparently a relationship similar to Eq. 2 is required in order to obtain the important quantity ν in Eq. 1. The form of this relationship can be derived if the unit shear process (passing of units of flow) is regarded as a chemical reaction, and if the equations well known to chemists are applied in connection with the rates of chemical reactions. It will therefore be appropriate at this point to examine these equations in some detail.

CHEMICAL THERMODYNAMICS AND THE RATES OF CHEMICAL REACTIONS

From thermodynamics we know that for a system in equilibrium—e.g., $A \rightleftharpoons B$ —the relative amounts of A and B present are given by

$$\frac{(B)}{(A)} = e^{-\Delta F/RT} \quad [3]$$

where (A) and (B) represent the amounts of A and B present, and ΔF is the change in free energy resulting from the change of one mol of A into one of B . Furthermore,

$$\Delta F = \Delta H - T\Delta S \quad [4]$$

where ΔH is the change in ordinary energy (heat of reaction) and ΔS is the change in entropy resulting when the same change occurs. We can thus write

$$\frac{(B)}{(A)} = e^{\Delta S/R} e^{-\Delta H/RT} \quad [5]$$

The true significance of this phenomenological description of an equilibrium in terms of the factors $e^{\Delta S/R}$ and $e^{-\Delta H/RT}$ is made possible by statistical mechanics, and that very simply and directly. The term $e^{-\Delta H/RT}$ is a consequence of the well-known Boltzmann relation, which states that when any body is considered as made up of a large number of particles having a definite total energy and an absolute temperature T , the relative probability that any particle is in an accessible state* having an energy ϵ is given by $e^{-\epsilon/kT}$ where k is a universal constant known as the Boltzmann constant.† Then if the average energy of the molecules of B is higher by $\Delta\epsilon$ per molecule than that of the molecules of A , and if the states of B are accessible to those of A , the relative amounts of B and A present must be proportional to $e^{-\Delta\epsilon/kT}$. Since $H = N\Delta\epsilon$ and $R = Nk$, where N is the number of molecules in a mol (Avogadro's number), this

factor can be written as $e^{-\Delta H/RT}$, as given in Eq. 5.

The significance of the term $e^{\Delta S/R}$, on the other hand, can best be brought out by an example. Suppose the state A corresponds to molecules of a perfect gas moving in a box at sea level and that the state B corresponds to the molecules in a second box at an altitude of h centimeters above sea level and having the same volume as the first box. Let the two boxes be connected by means of a pipe so that the molecules can easily get from one box to the other. (The significance of the term "accessible" should now be clear.) Then, according to the Boltzmann equation, the ratio of the number of molecules in B to that in A is given by $e^{-\Delta\epsilon/kT}$, where $\Delta\epsilon$, the difference in energy of a molecule in A and one in B , is equal to mgh , m being the mass of a molecule and g being the acceleration due to gravity. Thermodynamically,

$$\frac{(B)}{(A)} = e^{-Nmggh/RT} \quad [6]$$

and for the reaction, one mol of gas in box $A \rightarrow$ one mol of gas in box B , we see from Eq. 3 that $\Delta F = Nmggh = Mgh$ per mol, where $M = Nm$ = the molecular weight of the gas. Since this obviously corresponds entirely to a change in energy, $\Delta F = \Delta H = Mgh$ and $\Delta S = 0$. Now suppose the upper box has a volume three times that of the lower one instead of equal to it. We must, then, multiply the relative probability of B by 3, since each molecule now has three times as much space, or freedom, in B as in A . Thus,

$$\frac{(B)}{(A)} = 3e^{-Mgh/RT} = e^{1.099-Mgh/RT} \quad [7]$$

and

$$\begin{aligned} \Delta F &= Mgh - T(1.099R) \\ \Delta S &= 1.099R \\ \Delta H &= Mgh \end{aligned}$$

On the other hand, if B had only one-third the volume of A , the result would be $\Delta H = Mgh$ and $\Delta S = -1.099R$.

* The significance of the term "accessible" will be brought out below.

† For derivations of the Boltzmann equation, see references 10, 11 and 12.

Hence the entropy change in a reaction is a measure of what may be called the relative freedoms of the reactant and product of the reaction: if ΔS is positive, the product has more freedom than the reactant, while if it is negative, there are restrictions imposed on the product that are not imposed on the reactant. Furthermore, the actual numerical ratio of these restrictions is given by $e^{\Delta S/R}$.

A striking illustration of the importance of the change in the entropy in determining the conditions of equilibrium is found in the denaturation reactions of proteins (the kind of reaction that occurs when an egg is boiled or when a man is shot dead). Here, entropy increases of the order of 100 cal. per mol per deg. C. are observed, which corresponds to $e^{\Delta S/R} = 10^{22}$. That is, the denatured protein molecule can do something like 10^{22} as many things as the undenatured molecule. This tends to make the equilibrium shift in favor of the denatured molecules at very *low* temperatures. On the other hand, ΔH for these reactions is also large—the denatured molecule being less stable by something of the order of 100,000 cal. per mol—and this tends to make the equilibrium shift only at very *high* temperatures. The result of the operation of these two factors in opposite directions is that the equilibrium shifts from one side to the other very rapidly at ordinary temperatures—often within a range of a few degrees centigrade. It also makes the equilibrium very sensitive to small changes in other external conditions, and probably causes much of the great complexity shown in the behavior of living matter. It is evident, then, that the large entropy and heat changes occurring in protein denaturation reactions can furnish valuable clues to the answer to the question—so vital to everyone—of what happens during denaturation.*

* Although this is hardly the place for a discussion of this problem, it might be mentioned that the best interpretation of these

Large entropy effects are encountered in the flow of polymers¹³ and, as will be shown later, in the flow of solid metals; here they furnish important clues concerning the mechanism of the processes with which they are associated.

All that has been said in the preceding pages has referred to the properties of matter in equilibrium. This, of course, is the limitation that always is imposed on thermodynamics, but the more intimate view of the behavior of matter provided by statistical mechanics has been utilized by Eyring to make possible a thermodynamical treatment of molecular processes occurring at a constant rate and hence not restricted to matter in equilibrium.^{14,15}

Looking at the "energy map" of a typical chemical reaction (Fig. 3), we may say that the rate at which reactants go to form products (i.e., the rate of the reaction) is given by KN , where N is the number of molecules which in one second move in the direction corresponding to reaction past the point marked *activated state* (i.e., past the highest point on the easiest path from reactant to product) and K represents the fractions of these molecules that ultimately become product molecules. Unless the topography of the energy map is complicated by tortuous weavings or certain other features, none of which are at all likely to be encountered here, K is very close to unity, so can be neglected.

Eyring has calculated N by regarding a molecule in the activated state (an "activated complex," as he calls it) as nothing more than an ordinary molecule, save only that this molecule behaves strangely along the normal coordinate of its motion corresponding to its "reaction coordinate" (i.e.,

large numbers is that a protein molecule, when undenatured, probably has a very regular and definite structure. By breaking a few of the bonds suitably located in this structure (this requiring a lot of energy), the regular structure can give way to a myriad of possible structures whose very great number accounts for the large entropy increase.

the coordinate, motion along which corresponds to reaction; the abscissa of Fig. 3). Then N is the number of activated complexes multiplied by the rate at which each

inverse of the time for a single molecule to react.

The value of this formulation of reaction rates lies in the fact that ΔF^* is subject to

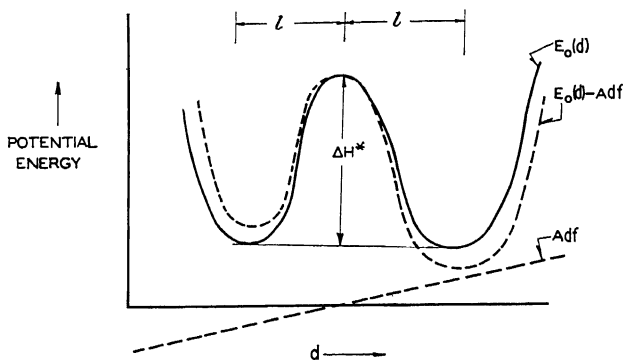


FIG. 4.—POTENTIAL-ENERGY CURVE FOR UNIT SHEAR PROCESS.

passes the point P in Fig. 3 moving in the direction corresponding to reaction. But as long as the activated complex is in equilibrium with the reactants A , thermodynamics can be applied, and it will be true that

$$\frac{\text{Number of activated complexes}}{\text{Number of reactant molecules}} = e^{-\Delta F/RT} \quad [8]$$

where ΔF is the free energy of activation of a mol of reactant molecules. This ΔF includes the properties of the activated complex along the reaction coordinate; if the part of ΔF depending on these properties is separated, and if a more or less straightforward statistical mechanical calculation of the rate of passage of molecules past P is carried out, it is found that

$$N = \frac{kT}{h} e^{-\Delta F^*/RT} \quad [9]$$

where ΔF^* is now the free energy difference per mol between the reactant and the activated complex when the latter is regarded as an ordinary molecule, except that the degree of freedom corresponding to the reaction coordinate has been disregarded, it having been absorbed in the factor kT/h . For our purposes, Eq. 9 gives the rate of any reaction in units of the

the same sort of interpretation for reaction-rate theory as ΔF was for equilibrium theory. It can be broken up into ΔH^* and ΔS^* , the heat and entropy of activation, each of which can tell a great deal about reaction mechanisms, just as ΔH and ΔS tell a great deal about what happens in many equilibria (e.g., in the denaturation of the proteins, as shown above).

APPLICATION OF EQUATION 9 TO THE PROBLEM OF SHEAR RATES

We are now ready to return to the problem proposed on page 59—to calculate the number of jumps in a given direction that a unit of flow can make in one second. Suppose the energy map for a unit shear process is that shown as $E_0(d)$ of Fig. 4. Here, d is the distance in the shear direction moved by units with respect to one another. The rate of passage of units past one another in either direction will then be

$$n = \frac{kT}{h} e^{-\Delta F^*/RT} \quad [10]$$

where ΔF^* is the difference in free energy of the units of flow in the normal and activated states. (If k is in ergs per degree and h is in erg-seconds, n is the number of passages per second of one unit past other

units.) In the absence of applied shear forces, the number of jumps, n_+ , in the positive d direction (that is, resulting in shear in the same direction as that shown by the arrows in Fig. 2) will be the same as that, n_- , in the negative d direction, and there will be no net shear. But if a shear stress f per unit area is applied in the positive d direction, the potential energy curve $E_0(d)$ of Fig. 4 will be modified, taking on instead the shape of the dotted line, with the form $E_0(d) - Adf$, where A is the projected area of each unit of flow in the shear plane (i.e., the area on which f acts, so that Af is the actual force acting on each unit of flow, and Adf is the linear potential field due to the shear force).

The number of jumps of units of flow per second in the positive direction with respect to one another will now no longer equal the number in the negative direction, since the activation energies for the two directions are no longer equal. Instead, the activation energy for motion in the positive direction will be lowered by an amount Af per molecule, while that in the other direction will be raised by the same* amount (l being the distance through which the shear stress acts in carrying the unit of flow from the normal to the activated state).

Then

$$n_+ = \frac{kT}{h} e^{-\Delta F^*/RT} e^{Af/kT} \quad [11]$$

and

$$n_- = \frac{kT}{h} e^{-\Delta F^*/RT} e^{-Af/kT} \quad [12]$$

and ν , the net number of jumps in the plus direction per unit of flow per second is

$$\begin{aligned} \nu &= n_+ - n_- = \frac{kT}{h} e^{-\Delta F^*/RT} \\ &\quad (e^{Af/kT} - e^{-Af/kT}) \quad [13] \\ &= 2 \frac{kT}{h} e^{-\Delta F^*/RT} \sinh(Af/kT) \quad [14] \end{aligned}$$

* This is only approximately true, and that for small stresses. See p. 64.

Substituting in Eq. 1,

$$\text{shear rate} = s = \frac{2\lambda}{L} \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \sinh(Af/kT) \quad [15]$$

(Note that ordinarily, $L = 2l$.) This is the general equation for shear developed by Eyring.

If $Af \ll kT$ (that is, if the energy supplied by the action of the shear force in aiding a unit of flow is small compared with its thermal energy), since $\sinh x \cong x$ for small values of x ,

$$s = \frac{2\lambda A}{Lh} e^{\Delta S^*/R} e^{-\Delta H^*/RT} f \quad [16]$$

That is, the shear rate is proportional to the shear stress. This constitutes ordinary viscous or Newtonian flow, such as is exhibited by water, and the coefficient of viscosity is given by

$$\eta = \frac{f}{s} = \frac{Lh}{2\lambda A} e^{-\Delta S^*/R} e^{\Delta H^*/RT} \quad [17]$$

This equation has been applied by Eyring and co-workers to the flow of ordinary liquids, with many interesting results.^{13,16-19}

If, on the other hand, $Af \gg kT$ (if the energy supplied by the shear force in activating the molecule is much larger than the thermal energy; also, if for any reason* n_- has a much smaller value than that given in Eq. 12),

$$s = \frac{\lambda}{L} \frac{kT}{h} e^{\Delta R^*/R} e^{-\Delta H^*/RT} e^{Af/kT} \quad [18]$$

which leads to the well-known law for the creep rates of metals:

$$\log s = C + Df \quad [19]$$

C and D being constants at any given temperature and for any given material.†

* See Discussion of Theory.

† The hyperbolic sine law for creep rates has been suggested previously on phenomenological grounds (e.g., by Nadai, in the S. Timoshenko 60th Anniversary Volume, p. 165), but there is little available experimental evidence for testing it. It is apparent that for substances

DISCUSSION OF THE THEORY

Before applying Eq. 15 to some actual experimental data, it will be well to investigate some of the possible difficulties that might arise from such an application. We may say at the outset that the theory is particularly designed for the interpretation of shear processes that require

between a few molecules or from some more complicated mechanism. The usefulness of the theory lies in the fact that by fitting it to experimental data it is possible to get some idea of the magnitudes of ΔH^* , ΔS^* and Al , while from these in turn something may be learned concerning the fundamental mechanism of the flow.

One of the difficulties that might be encountered in the application of the theory entails the measurement of the true value of the shearing stress f , which acts on the unit of flow. Is this stress the same as σ , the macroscopically measured shearing stress? For the sake of generality, we may say that

$$q\sigma = f \quad [20]$$

where q is a stress-concentration factor similar to that required in calculating the breaking strengths of crystals.

In the derivation of Eq. 15, it was stated that the activation energy for jumping in one direction is raised by an amount Alf , while for the opposite direction it is lowered by the same amount. This is not strictly true, however, since the addition of a linear potential field due to the force shifts the minima and maximum of the resultant field in such a way that the distances through which the force must act in going from the two normal states to the activated state are not the same. This is made clear by Fig. 5a. The effect will be most pronounced when the top of the potential barrier has a small curvature (Fig. 5b), and will show up experimentally in the impossibility of finding a constant, a , that will give a linear plot of the creep rate against $\sinh a\sigma$. In general, however, this effect can be said to be unimportant, since the shifts that do occur should be of the same order of magnitude as the elastic strain in the specimen under the given stress, and elastic strains are usually small (of the order of tenths of a per cent for the macroscopic stresses met with here). And if the effect is important, but the stresses are so large that the range where $\sinh a\sigma \cong e^{a\sigma}/2$ is entered, the variation in l with the stress can be determined, since it is still true that

$$\left(\frac{\partial \ln (\text{rate})}{\partial \sigma} \right)_T = \frac{qAl}{kT} \quad [21]$$

If the situation of Fig. 5b holds, the hyperbolic sine law will be drastically wrong, but if l

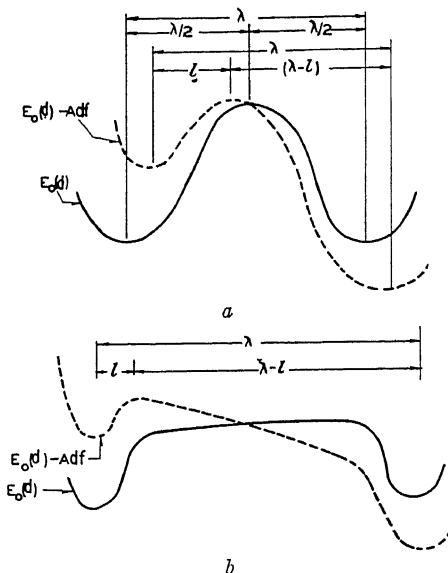


FIG. 5.—POTENTIAL-ENERGY CURVES FOR UNIT SHEAR PROCESSES.

Illustrating possible causes for deviation of rate of flow from a hyperbolic sine law at large stresses.

some activation energy in order for flow to occur. Concerning the nature of the unit of flow and of the energy barrier restricting flow, there are no serious limitations, and the theory is quite general: the unit of flow may be a single molecule or a group of many molecules, and the barrier may arise directly from the repulsions

in which the molecule is the unit of flow, since Al for molecules is of the order of 10^{-22} c.c. (corresponding to a mol volume of 60 c.c.), a good test for the hyperbolic sine law would be obtained for stresses such that $f \times 10^{-22}/2kT$ is of the order of unity. At $T = 300^\circ\text{K}$. (room temperature) this corresponds to shear stresses of the order of 1000 kg. per sq. cm. Clearly, such materials as water cannot be studied under such high shear stresses. Glasses, however, might be subjected to such stresses, and so make possible an experimental test of the hyperbolic sine law of shear rates.

is not very dependent on the stress in the range used, Eqs. 21 and 19 will tend to be more valid than Eq. 15, even down to relatively low stresses; that is, the logarithmic creep law will be more nearly correct than the hyperbolic sine law even in the range where $qA\sigma$ is small compared with kT .

Next comes the possibility that the shear stress can also act in some ways other than that proposed by the present theory in influencing the rate of shear. Thus Kanter³ has postulated some effect of the stress on the entropy of activation ΔS^* , and Becker⁴ has suggested that ordinary viscous flow (rate of flow proportional to the shear stress) is caused by a proportionality between λ , the distance jumped by a unit of flow, and the shear force. Neither of these effects appears to have much physical significance. Thus it is difficult to conceive any mechanism whereby a stress can have as marked an effect on the entropy of a regular lattice as that required here; and as to Becker's suggestion, the explanation of ordinary viscous flow afforded by Eyring's formulation appears to be far more likely, since the distance jumped by a unit of flow should be related to a lattice distance, and lattice distances are known to be very insensitive to applied stresses.

A test of the validity of the assumption that the stress affects the shear rate chiefly through the addition of a linear, unsymmetrical potential field to an otherwise symmetrical potential energy barrier might be found in a comparison of the creep rates for specimens in tensile, torsional, and compressional stresses. In tension and compression, stresses would act normal to the shear plane as well as in it, while in torsion there need be no such stresses. If the shear rate were the same in all, the effect of stresses in other ways than we have pictured would be shown to be small.

Another test might be in the measurement of creep rates in tensile tests on single crystals that have their most important glide planes oriented in different directions with respect to the direction of the applied tensile stress. If, for a given shearing stress resolved along the glide direction in the glide plane, the shear rate in that direction is found to be independent of the orientation of the plane with respect to the tensile stress, our contention will have been proved. Rough measurements indicate that this is true.²⁰

In the derivation of Eqs. 15 to 18 it has been assumed that shear occurs only by the operation of a single molecular mechanism. Clearly, this need not be true, and in a given specimen many widely different mechanisms (such as slip along different slip planes, and flow by the self-diffusion of single atoms) will always be operating simultaneously, each having its own characteristic value of l , λ , L , ΔS^* , ΔH^* , A , and q . Thus, in general,

$$s = \sum_i \frac{2\lambda_i kT}{L_i h} e^{\Delta S^*_{i/R}} e^{-\Delta H^*_{i/RT}} \sinh(q_i A_i l_i \sigma / kT) \quad [22]$$

where the sum is over all of the possible mechanisms. Usually only one of the mechanisms (i.e., only one of the terms in Eq. 22) will account for the greater part of the observed rate. It is entirely possible, though, that a single term will not give a major part of the shear rate under all conditions: under small stresses, for example, one mechanism may account for most of the creep, while under large stresses another mechanism may be more important. Each mechanism, however, contributes *something* to the total observed shear rate under all conditions. A very interesting example of this operation of more than one shear mechanism has been found by Chalmers in the creep of single crystals of tin, and will be discussed later.

Allied to this generalization of the simultaneous operation of many different shear mechanisms is the question of the interpretation of strain-hardening and crystal regeneration (*Erholung*) in terms of the present theory. These phenomena, which with the shear rate determine the shape of the stress-strain diagram usually used in describing crystal plasticity, are the result of the dependence of the constants in Eq. 22 on time and on total strain. Thus hardening would result from an increase in ΔH^* or from a decrease in ΔS^* , q , A , or l , while regeneration would result from changes in the opposite direction. Indeed, a study of the dependence of these constants on time and on strain would probably furnish a valuable clue to the nature of the molecular processes occurring during strain-hardening and *erholung*.

It might be objected that the present theory overlooks the possibility that the observed creep rates of metals may be due to an equi-

librium between the rate of *erholung* or annealing of the metal and its rate of strain-hardening. Such a mechanism of creep has indeed often been suggested. A little consideration will show,

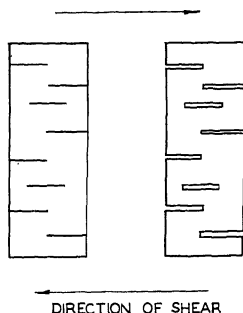


FIG. 6.—ILLUSTRATING REQUIREMENT THAT SHEAR OCCUR ACROSS AN ENTIRE CROSS SECTION OF A BODY IN ORDER THAT STRAINS LARGER THAN ELASTIC STRAINS CAN BE OBSERVED.

however, that this theory can really be included in our general treatment. Suppose that only structures of a type B in a metal can give rise to shear, but that when such a "B structure" undergoes shear it is converted into an "A structure," which cannot undergo shear, so that hardening results. But A structures can spontaneously go over into new B structures by the process of *erholung*. Then if the rate of formation of A structures from B structures is large compared with the reverse process, the rate of shear will be determined by the rate of the *erholung*. We have supposed that the *erholung* process by itself does not result in shear; its rate cannot then be affected by the action of shearing stresses, and the result should be a creep rate independent of the stress. These are commonly not observed, although one possible example may appear later on. If, on the other hand, the *erholung* did result in shear, its rate could be treated by means of Eqs. 15 or 18.

Before examining available data in the light of Eqs. 15 and 18, it might be well to mention one feature of shear that must be kept in mind, particularly when studying crystalline solids: When a plane along which shear occurs has an area A , and when shear amounting to δ occurs over only a small portion of this plane having an area a , the macroscopically observed shear over

the entire area A will *not* be given by $\frac{a}{A} \delta$.

The release of shear stress in a part of a shear plane can only give rise to an observable shear corresponding to an elastic strain over the remainder of the plane. To illustrate this, suppose that in the bar pictured in Fig. 6a a shearing motion amounting to δ_0 cm. has occurred over half the area of each of n planes making an angle of 90° with the axis of the bar. Suppose that by virtue of this motion all of the shearing stress has been released over these regions. Then the lateral displacement of the ends of the bar in the direction of the shear stress will not be given by $n\delta_0/2$, but instead will be given by the elastic shear strain of a bar from which these portions of released stress have been cut out (Fig. 6b). Since elastic strains are always small, large plastic shear (from, say, a small percentage up to the large percentages that may be observed in single crystals) can only result from a shear all of the way across the cross section of the bar.

The significance of this fact is that if potential units of flow are not suitably distributed through a shear plane, their movement cannot result in the expected macroscopically observable shear. In liquids and even in amorphous solids, this requirement is unimportant, since it is readily fulfilled by the mobility of the molecules and the homogeneity of the material. Crystalline solids, however, probably are not homogeneous, and their constituent atoms and molecules are not very mobile. Potential units of flow probably are scattered relatively sparsely throughout the specimen. Therefore, this requirement is likely to play an important role in determining the rate of flow of solids.

APPLICATION OF GENERAL THEORY TO AVAILABLE DATA ON CREEP OF METALS

In the following pages an attempt will be made to interpret some of the available

experimental data on the flow of crystalline metals in the light of the general equations. The rate of shear of a crystalline metal is measured usually by determining the rate at which a bar under tensile stress increases in length; the time rate of increase of tensile strain (i.e., the creep rate), $u = \frac{d\epsilon}{dt}$ (where ϵ is the elongation per unit length), is related to the shear, γ_{\max} , occurring along the plane of maximum shear stress by²¹

$$u = \frac{2}{3} \frac{d\gamma_{\max}}{dt} \quad [23]$$

while the shearing stress, σ_{\max} , in this plane in terms of the tensile stress τ is

$$\sigma_{\max} = \tau/2 \quad [24]$$

Substituting Eqs. 23 and 24 in Eq. 18, the relationship between tensile stress and creep rate becomes:

$$u = \frac{2\lambda}{3L} \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} e^{qAl\tau/2kT} \quad [25]$$

Creep rates have also been measured with tests in torsion.³¹ In this case the torsional creep rate is given directly by Eq. 18, where σ is the applied torsional stress.

In single crystals, where shear can occur in various glide planes that make angles ϕ_1, ϕ_2, \dots with the direction of the tensile stress, and along different glide directions in these planes which make angles ψ_1, ψ_2, \dots with the projection of the direction of the tensile stress in the glide plane, the tensile creep rate will be the resultant of several simultaneous mechanisms. Remembering that the resolved shear stress σ_i for one of these glide systems is related to the tensile stress τ by

$$\sigma_i = \frac{\tau}{2} \sin 2\phi_i \cos \psi_i \quad [26]$$

and that the amount of shear γ_i in such a system results in a contribution to the tensile creep of amount

$$\epsilon_i = \gamma_i \cos \phi_i \cos \psi_i \quad [27]$$

we see that the total tensile creep of a single crystal is given by

$$u = \sum_{\text{all glide systems, } i} \cos \phi_i \cos \psi_i \frac{\lambda_i}{L_i} \frac{kT}{h} e^{-\Delta F^*_i/RT} e^{qA_i\tau/2kT} \quad [28]$$

where $\lambda_i, L_i, \Delta F^*_i$, etc., are the quantities typifying each glide system. If tests are carried out on any one single crystal, presumably most of the creep will usually result from the slip occurring in one glide system, and only one term of Eq. 28 will be required to describe the creep behavior of the particular crystal. This may not, however, be true at all temperatures and at all stresses for a given crystal, and in crystals with different orientations with respect to the tensile stress, different glide systems will operate in general.

In order to evaluate the constants appearing in Eq. 18, the data employed must include measurements of creep rates for a range of stresses at each of several temperatures. The procedure that has been used here is illustrated by Fig. 7. using the data of Chalmers²² and Tyte²⁶ on tin. The logarithm of the steady-state creep rate at a given temperature is plotted against the stress, and from the slope of this plot, which usually is a straight line, can be derived a value of qAl . By extrapolating the straight lines back to zero stress, the values of the logarithms of

$$\frac{2}{3} \frac{\lambda}{L} \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

are then found for each temperature.* These in turn are plotted against $1/T$ to give values of ΔH^* (from the slope of the resulting straight

* The validity of this extrapolation has nothing at all to do with the question of whether there is a finite creep rate at zero stress; the extrapolation is merely a convenient mathematical method for evaluating the quantity $\frac{2}{3} \frac{\lambda}{L} \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$ at the temperature in question.

line) and of

$$\frac{2}{3} \frac{\lambda}{L} \frac{kT}{h} e^{\Delta S^*/R}$$

(from the intercept of the straight line at

cannot be further resolved to give individual values of q , A , l , λ , L and ΔS^* . But even this incomplete evaluation of the constants is very useful in understanding the creep mechanism in metals.

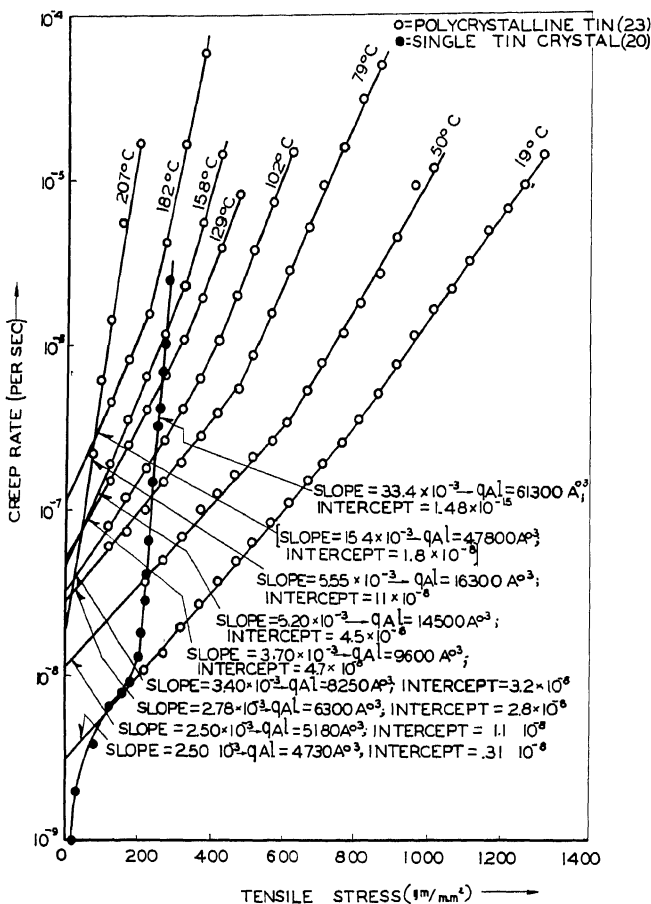


FIG. 7.—CREEP BEHAVIOR OF TIN.^{22,26} METHOD OF EVALUATING qAl FROM OBSERVED DATA.

$1/T = \infty$, the variation of the factor kT/h with temperature being negligible compared with that of the factor $e^{-\Delta H^*/RT}$ in the same range, so that kT/h may be regarded as a constant, with T the mean temperature in the range). This is, of course, as far as we can go in determining the constants from the experimental data; the factors qAl and

$$\frac{\lambda}{L} e^{\Delta S^*/R}$$

The greatest difficulty in this procedure is to obtain data sufficiently accurate to give reasonably smooth curves when the logarithm of the rate is plotted against the stress, and more especially, when the logarithm of the rate intercept at zero stress is plotted against $1/T$. The latter plot, particularly, is likely to be erratic, so that the values of ΔH^* and $\frac{\lambda}{L} e^{\Delta S^*/R}$ obtained are not as reliable as the values of qAl , although their orders of magnitude are

certainly correct in most cases, and this is what is most important at present.

Concerning the factor λ/L , it would be expected that ordinarily this should be of the order of magnitude of unity. Any marked

Chalmers' data on the creep of single crystals of tin, it has been assumed that $\phi = 45^\circ$ and $\psi = 0^\circ$, as this was indicated by him to be nearly true. Owing to the large number of equivalent glide systems in tin,

TABLE I.—Data on Different Materials

| Number of Curve Giving qAl in Fig. 9 | Substance | Reference No. (Page 81) | ΔH^* , Cal. per Mol | ΔS^* , Cal. per Deg. per Mol | ΔF^* , Cal. per Mol, at | |
|--|--------------------------------------|-------------------------|-----------------------------|--------------------------------------|---------------------------------|---------------|
| | | | | | 1000°K. | 300°K. |
| 1a | Tin, single crystal | 22 ^b | | | | |
| 1 | Lead | 23 | 3,800 | -99 | 103,000 | 37,500 |
| 2 | Lead | 24 | 2,300-8,400 | -93 to -83 | 95,000-91,000 | 30,000-33,000 |
| 2a | Lead | 25 | 13,000 | -74 | 87,000 | 35,000 |
| 3 | Tin, polycrystalline | 26 | 5,350 | -80 | 85,000 | 29,350 |
| 4 | Zinc, High-Grade | 27 | 31,400 | -1 | 32,000 | 31,000 |
| 5 | Zinc, Brass Special Grade | 27 | 16,500 | -49 | 65,000 | 31,000 |
| 6 | 60-40 brass | 28 | 15,300 | -76 | 91,000 | 38,000 |
| 7 | 0.4 % C steel | 29, p. 244 | 28,500 | -75 | 103,000 | 51,000 |
| 8 | 0.5 % Mo steel (0.5 % Mn, 0.25 % Si) | 29, p. 72 | 45,000 | -55 | 100,000 | 62,000 |
| 9 | 0.34 % C steel | 30 | 26,300-29,400 | -60 to -52 | 86,000-81,000 | 44,000-45,000 |
| 10 | 0.5 % Mo steel (0.2 % Mn, 1.4 % Si) | 29, p. 78 | 17,000-21,000 | -90 to -86 | 107,000 | 44,000-48,000 |
| 11 | 18 % Cr, 10 % Ni steel | 29, p. 216 | 5,000-15,000 | -97 to -108 | 112,000 | 37,000-46,000 |
| 12 | Cast steel | 31 | 102,000 | +14 | 88,000 | 98,000 |
| 13 | C steel | a | 60,100 | -42 | 102,000 | 73,000 |
| 14 | C-Mo steel | a | 41,500 | -60 | 102,000 | 59,000 |

^a Data obtained from Mr. N. L. Mochel, of the South Philadelphia Works of the Westinghouse Electric and Manufacturing Co., and from Mr. P. G. McVetty and Mr. D. W. Gunther, of the Westinghouse Research Laboratories. The author wishes to express his thanks for the opportunity to use these data.

^b The data used here were given as a plot of creep rate against stress in Fig. 3 of this reference, but the scale of stresses in this plot is obviously in error. From the context of the article, however, it is probable that the zero point and the point marked 100 gm./mm.² are correct, so in using these data, the rest of the scale was taken to conform to these two points.

deviation from this, as from a wide spacing of the glide planes ($L \gg \lambda$), can best be regarded as an entropy effect, reflecting, say, a sparse concentration of the units of flow. Therefore, we can regard it as true that $L \cong \lambda$ and write $\Delta S^* = R \log_e \left(\frac{\lambda}{L} e^{\Delta S^*/R} \right)$, where ΔS^* now includes a possible concentration effect.

The values of ΔH^* and ΔS^* , and values of ΔF^* at 300°K. and 1000°K. derived from these, for a number of different materials for which creep data are available, are given in Table I. The values of qAl were found to be strongly dependent on the temperature in most cases, so these are plotted semilogarithmically against the temperature in Fig. 8. For all of the polycrystalline materials represented here, the creep rates used were the so-called "second-stage" creep rates, but for the tin single crystals initial creep rates were employed.

In the values of qAl and ΔF^* , from

one at least will find itself nearly so oriented, so will cause most of the observed creep.

INTERPRETATIONS OF THE DATA

The data summarized in the preceding paragraphs nearly all show the same general characteristics. Taking these characteristics as typical of metallic crystalline flow in general, we shall now try to understand their significance in terms of a general molecular picture. An attempt will also be made at interpreting some of the less general features associated with metallic flow, such as the reason for the much greater softness of lead than of iron, and for the great softness of single crystals; the nature of the microcreep found by Chalmers in single tin crystals; the possible effects of grain boundaries and impurities; the role of self-diffusion in creep; and creep at very low temperatures. It must be understood, however, that some of the

interpretations advanced are somewhat speculative, particularly with respect to the less general characteristics mentioned above, and that sometimes they are made

value of qAl found for all of the metals. Thus, if $q = 1$ (no stress concentration), and if A is the cross-sectional area of a single metal atom, and if l is one lattice

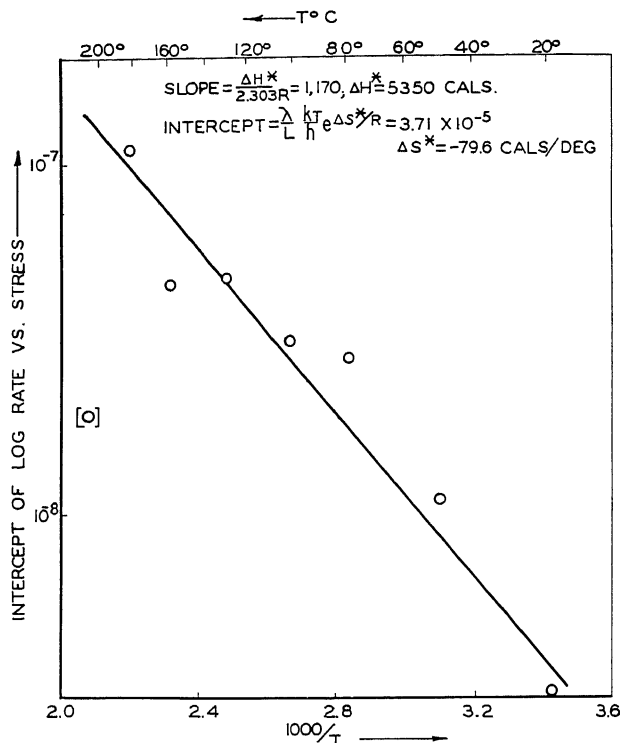


FIG. 8.—CREEP BEHAVIOR OF TIN.^{22,26} METHOD OF EVALUATING ΔH^* AND ΔS^* FROM OBSERVED DATA.

on the basis of rather meager shreds of experimental evidence. But the purpose of the present paper is predominantly to illustrate the nature of the information derivable through the application of Eqs. 15 and 18 to suitable experimental data rather than to develop any concepts that must be regarded as very definite with regard to metallic flow. So perhaps this is excusable, especially in the light of the fact that the speculations are capable of rather direct verification or disproof, as the case may be, through suitably designed experiments.

One of the most striking characteristics of the experimental data is the very large

distance in a crystalline metal, values of qAl of something like 10 \AA^3 would generally be found for metals ($1 \text{ \AA} = 10^{-8} \text{ cm.}$). Instead, values 100 times or more as large are usually found. *It is this large value of qAl , together with the large stresses required to give rise to detectable rates of flow, that causes the creep of metals to depend upon the stress exponentially rather than linearly.*

The second striking feature in the experimental data is the generally very small value of $\frac{\lambda}{L} e^{\Delta S^*/R}$. Ordinarily it would be expected that if L and λ corresponded to lattice distances, ΔS^* would be close to zero, and certainly no larger than ± 10 .

Instead large negative values are found in the neighborhood of 50 to 100 cal. per degree per mol in 12 cases out of 14, corresponding to values of $\frac{\lambda}{L} e^{\Delta S^*/R}$ of about 10^{-10} to 10^{-20} .

These two facts could perhaps be explained if the unit shear processes occur only at points of great stress concentration (q of the order of several hundred), and if this unit process were a simple passage of metal atoms by one another as in self-diffusion. Such an interpretation is supported by the fact that ΔH^* is found to be usually of the same order of magnitude as the activation energies of diffusion processes in solid metals. The very small value of $\frac{\lambda}{L} e^{\Delta S^*/R}$ might then be a consequence of the small number of points at which the value of q is as large as it is found to be here, since for the reasons discussed on page 66, in order for flow to occur at all in a given plane, units of flow must be properly distributed all over the plane, and owing to their scarcity here, this is very improbable of occurrence, so that $e^{\Delta S^*/R}$ is very small.

This last argument, however, is not at all convincing, although it seems necessary if the explanation for the large value of qAl is taken to be associated with a large value of q and if the observed values of ΔS^* are to be accounted for. The proper distribution of sites of unit shear processes requires that nearly every lattice site in a given shear plane at some time be the location of a unit shear process. This means that the points of stress concentration must readily wander over the given shear plane, since a concentration on the order of one-hundredfold is utterly impossible at all points simultaneously. This is in turn highly unlikely, since such concentrations of stress as do occur are probably produced by cracks and other similar immobile features.

It might also be suggested that in polycrystalline material the rate of shear is

governed by the shear of those crystals that are least favorably oriented with respect to the tensile stress. The surrounding crystals will then be continually relaxed and the stresses would concentrate on the few unfavorably located crystals. Evidently something like one crystal in one hundred must be so oriented in any given cross section for this explanation to apply. The difficulty here is twofold: first, the even larger qAl value of single crystals of tin must be explained, and second, unless the unfavorably oriented crystals form some kind of interlocking network among themselves (which is highly improbable), they will affect the creep rate of the specimen in the same way as the addition of one per cent or less of sand to water affects the viscosity of the water (an effect that is very slight).

Finally, it is not readily understood why stress concentrations should depend so strongly on the temperature as the behavior of qAl would indicate.

The conclusion thus seems inescapable that the large value of qAl cannot arise from a large value of q , and it will in fact probably be safe to take q as equal to unity.* That l could be large enough to account for the values of qAl is even less admissible, for it is inconceivable that an atom could in one leap move something like 100 lattice distances before arriving at the activated state.

There remains, therefore, only the possibility that the area A is much larger than the cross section of a single atom. This explanation is very attractive, since it is what we should expect if the unit shear process occurred through the formation of

* It does, however, seem very possible that large q values may be of some importance in determining the flow of polycrystalline materials immediately after loading, when there is probably a great stress concentration at a relatively few points in the material. These, however, are soon evened out by the plastic flow. It is interesting that correspondingly rapid initial creep rates do not seem to be observed in single crystals.

"dislocations" such as are illustrated schematically in cross section in Fig. 10 and have been employed previously by Taylor, Orowan, Polanyi and others to

Then if the lattice distance is λ , the area of the top of the block that undergoes shear due to the motion of the dislocation is $n\lambda d$, and the actual shear stress acting on the

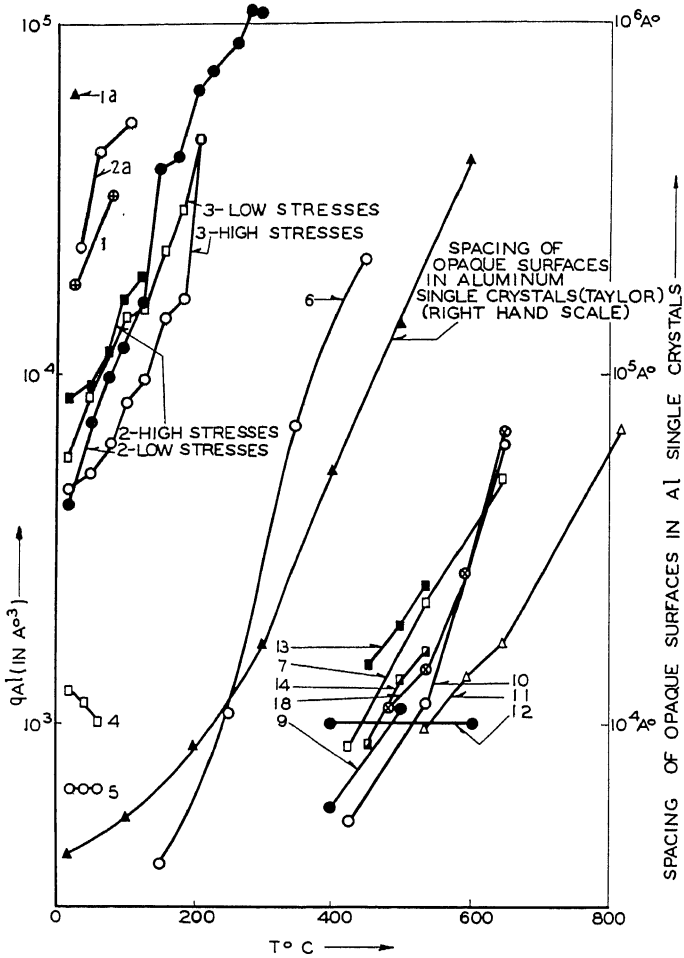


FIG. 9.—VALUES OF qAl FOR DIFFERENT METALS AT DIFFERENT TEMPERATURES. The key to the numbers is in Table 1. All the curves except the one marked by solid triangles correspond to the left-hand ordinate scale.

explain the plasticity of crystals. It must be emphasized that the regions of dislocation in Fig. 10 extend over a considerable distance in the direction perpendicular to the plane of the paper. Let us call this distance d . Suppose the block of material through which the dislocation travels in the plane of the paper is n atoms wide.

block is (assuming $q = 1$) $n\lambda d\sigma$. If at any instant the distance in the shear direction moved by a point on the upper surface of the block relative to that of a point on the lower surface of the block is μ , it can be said that $\mu \cong \lambda\alpha$, where α is the fraction of the distance through the block moved by the dislocation. A plot of the

energy against μ would then look like Fig. 11, and the flat part of the curve between $\mu = 0$ and $\mu = \lambda$ is very long compared with the rest of the curve when n is large; this corresponds to the dislocation when located inside the block. The energy basins, on the other hand, correspond to the dislocation when it is close to or at the surface of the block, and this in turn corresponds to values of μ of approximately λ/n ; that is, the distance through which the two parts of the block must be moved relative to one another in order to introduce a dislocation into the block is something like λ/n . The work done by the shear force in lowering the activation energy is thus approximately

$$(n\lambda d\sigma) \times (\lambda/n) = \lambda^2 d\sigma \quad [29]$$

and this must be equal to $qAl\sigma$. Since λ^2 is of the order of 10 \AA^2 and q is close to unity, and qAl usually has value of 1000 \AA^3 or more, d must be of the order of magnitude of 100 \AA . or more.

It is to be noted from Fig. 9 that the logarithmic rate of change of qAl with temperature is strikingly similar for nearly all of the metals—and this even when we have to deal with metals as widely different as iron and lead. This dependence of qAl on the temperature is best ascribed to a marked increase in d with increasing temperature; at higher temperatures much wider blocks are evidently involved in slip. This might be compared roughly to the effect of temperature on the separation of the surfaces that prevent the transmission of dislocations ("opacities") postulated by Taylor to account for strain-hardening, and would presumably arise in much the same way. It is interesting that if $q\lambda^2$ for single crystals of tin is taken to be 10 \AA^2 , d is found to be of the order of magnitude of 10^4 \AA , which is of the same order of magnitude as the separation of the surfaces of misfit found by Taylor for other single crystals. In Fig. 9 there has been included a plot of the temperature dependence of

this separation of the surfaces as found by Taylor for aluminum. The logarithmic rate of change of this separation with temperature is seen to be about the same as

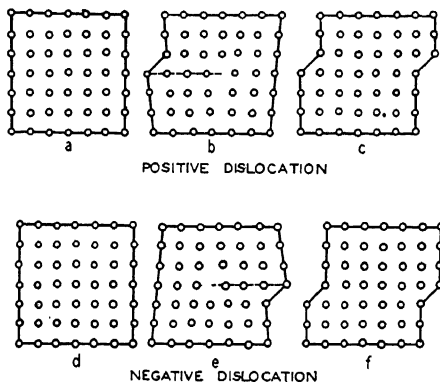


FIG. 10.—SHEAR OF CRYSTAL BY MEANS OF MOTION OF DISLOCATIONS.

that for qAl for most of the other metals. The conclusion might be that the same sort of barrier that stops the forward movement of dislocations also acts to prevent their extension in the direction perpendicular to their motion.

We come now to a consideration of the observed values of ΔH^* and ΔS^* . It seems fairly obvious that the energy required to form a dislocation of length d should, at least in part, be proportional to the length of the dislocation. That is,

$$\Delta H^* = \Delta H^*_0 + \Delta H^*_1 d \quad [i]$$

where ΔH^*_0 might be an energy associated with the strain occurring at the ends of the dislocation, and $\Delta H^*_1 d$ is the part of the energy depending on the length of the dislocation. As d is markedly dependent on the temperature, this should give rise to some dependence of the activation energy for creep on the temperature. To a rough first approximation, it is true for most of the metals considered here that qAl , and hence d , changes linearly with the temperature over the range of temperatures usually used. That is,

$$d = d_0 + d'T \quad [\text{ii}]$$

Substituting Eqs. i and ii in the creep equation, No. 18, we find

$$S = \frac{\lambda kT}{L h} e^{\Delta s^*/R} [e^{-\Delta H^* d_1/R}] e^{-\frac{\Delta H^* d_0 + \Delta H^* d_0}{RT}} \quad [\text{iii}]$$

That is, in addition to the constant factor

small (i.e., making for an apparently negative entropy of activation in Table 1) might be the following: It is very probable that dislocations occur most readily at only a very few places in an actual crystal (say at those positions at which ΔH^* is particularly low because of some lattice imperfection). Furthermore, because of the condition discussed earlier in this paper

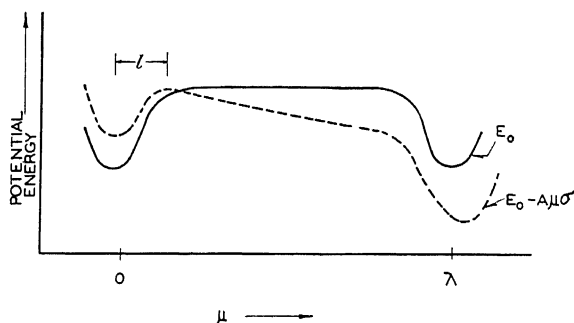


FIG. 11.—POTENTIAL-ENERGY CURVE FOR A DISLOCATION.

involving the entropy, there is a constant factor (shown in brackets in Eq. iii) involving the rate of change of activation energy with temperature. This factor will show up as an apparent negative entropy of activation.* Furthermore, the "activation energy," when determined as in this work, appears to be only $\Delta H^*_0 + d_0 \Delta H^*_1$, which is presumably much less than the true energy of activation. The temperature variation of the activation energy can thus be made, qualitatively at least, to account for both the very small activation energies and the negative "entropies of activation" that have been observed. A more quantitative analysis of the activation energy will be made at a later date, using equation i directly with values of d as estimated from observed values of qAL .

A further factor tending to make $\frac{\lambda}{L} e^{\Delta s^*/R}$

(p. 66), only when these imperfections are suitably distributed across a potential shear plane in the crystal can macroscopically observable shear occur in that plane. This means that only relatively few of the planes in the crystal can function as shear planes, so that L is much greater than λ ; this is probably the cause of distinct slip bands in a stressed crystal. If these bands are spaced by, say, 10^{-4} cm., and if λ is of the order of 10^{-8} cm., the factor λ/L would have a value of around 10^{-4} , giving a contribution to what is given as entropy of activation in Table 1 of something like -15 to -20 cal. per deg. per mol.*

* The results of D. Hanson and M. A. Wheeler³⁵ tend to indicate, however, that when a metal is allowed to creep slowly (under small stress) to a given extension (i.e., in long-time creep tests such as those from which the data used here were all obtained) slip bands are not observed even though they may form when a similar specimen is stretched rapidly to the same extension. Presumably, therefore, the bands are not so widely spaced under creep conditions, and this factor may be less important here.

* A similar apparent entropy effect is found in the study of the conductivity of ionic crystals, although here an increase in the temperature results in a decrease in activation energy, so gives rise to a positive "entropy of activation." See for example, F. Seitz: *Modern Theory of Solids*, 555. New York, 1940.

The general features of metallic flow thus seem to indicate that the flow occurs by means of dislocations which form at only relatively few points in the metal lattice, and whose lateral dimension depends strongly on the temperature, in a manner probably similar to that of Taylor's "opaque surfaces." We now turn to some more specific questions related to metallic flow.

First, why does solid lead, for instance, flow so much more easily than steel? Table 1 shows that for iron and steel at 1000°K. the values of ΔF^* , the free energies of activation for the unit shear processes, would be nearly the same for the two (assuming lead to remain solid at this temperature). Indeed, the values of ΔF^* are surprisingly similar for all metals at 1000°K. Therefore, the origin of the difference cannot lie here. Instead, we see that lead has a very much larger value of qAl than steel (Fig. 9)—perhaps 100 times as large at any given temperature. This, if what has been said above is true, is probably due to a much greater lateral extension of a region of dislocation in lead than in iron, which is, in turn due to the presence of fewer or less effective opaque surfaces. In fact, it seems to be true that the greater part (but not all) of the difference in the creep rates of solid metals at 1000°K. is due to this very wide difference in the values of qAl , hence of the lateral extension of dislocations, which they show at that temperature.

It is a well-known fact in metallurgy that soluble impurities cause a metal to harden much more than do insoluble, intergranular impurities. An explanation of this, perhaps, is to be found in the following: when a dislocation, on extending itself in a lateral direction (direction perpendicular to the plane of the paper in Fig. 10), meets a foreign atom, its progress in that direction is arrested. This tends to decrease A and perhaps also to increase ΔH^* , which in turn makes the material flow much more slowly

and thus become harder. An impurity at a grain boundary will be able to have no such effect. (The validity of this suggestion can be readily tested by means of appropriate experiments, of course.)

The available data on the creep rates of single crystals are inadequate for the complete application of Eq. 18. The measurements by Chalmers on tin crystals at room temperature, however, make it possible to find values for qAl and ΔF^* . These values can then be compared with the data of Tyte on polycrystalline tin (the effects of differences in purity being assumed, perhaps wrongly, to be small). It is found that qAl is about 10 times as large for single crystals of tin as for the polycrystalline tin at room temperature. On the other hand, ΔF^* is also somewhat larger for the single crystals.

The question is often asked: Would a perfect crystal be extremely soft or extremely hard? Is the ease of flow of single crystals a property that depends on structure imperfections, or is it a property of the perfect lattice? The answer to this question may be indicated in the facts mentioned above. The larger value of qAl in single crystals probably is due to the possibility that dislocations can extend over a much greater lateral distance, and the more perfect is the crystal, the greater should this distance be, since there will be fewer "opaque surfaces" to prevent the extension of dislocations. Yet, if dislocations can form most easily at only certain points of imperfection (and we have seen that this is likely), the number of these points will decrease as the crystal becomes more perfect. This will cause ΔS^* to become more negative and may also tend to increase ΔH^* , either or both of which will cause ΔF^* to increase. Whether or not a crystal will become more plastic as it becomes more perfect will then depend upon which of these two opposing effects will predominate in the process of approaching the perfect crystal. And although it would seem that a really perfect crystal should not be very plastic,

in actual practice $qAl\sigma$ (where σ has the value corresponding to the stresses ordinarily used) evidently increases somewhat more rapidly than ΔF^* , so that it appears, from experiments, that the more perfect a crystal is, the softer it becomes.

The temperature coefficient of creep is evidently a composite effect, since it arises as much from the existence of an activation energy for creep as from the great change in qAl with temperature. This means that if an attempt is made at evaluating the activation energy by using creep measurements at a single stress and different temperatures, a much larger energy will be found than is actually operative.

CREEP AND SELF-DIFFUSION

Chalmers, in his study of the creep rate of single tin crystals, was able to show that at low stresses in these crystals the creep rate is directly proportional to the applied stress, rather than to an exponential involving the stress, whereas at higher stresses (above about 200 grams per sq. mm.) the rate increases much more rapidly with the stress. Chalmers assumed that two different mechanisms were acting: he called the creep whose rate is proportional to the stress "micro-creep" and that which increased more rapidly "macro-creep." The question immediately arises, whether the two types of creep really involve different mechanisms or are merely the consequence of the hyperbolic sine law of Eq. 15. An attempt to fit Chalmers' data into a hyperbolic sine equation leaves no doubt of the correctness of his interpretation that there *are* two distinct mechanisms; we are clearly dealing with a case in which the total rate must be given by a sum of two separate rates, as in Eq. 22.

From the fact that the creep rate is proportional to the applied stress, and knowing the range of stresses for which this is true, we can place an upper limit on the value of qAl which characterizes this type of creep. (The problem is simply to find the

largest possible value of a that in a given range of values of x will enable $\sinh ax$ to be very nearly proportional to x .) It turns out that qAl must be no greater than 5000 \AA^3 , or about one-tenth of its known value of $63,600 \text{ \AA}^3$ for macrocreep. This is still a large value, but is it not possible that its actual value is something closer to the much smaller one ($\sim 15 \text{ \AA}^3$), which would correspond to single atoms acting as units of flow? That is, it is quite possible that microcreep occurs simply by the same process as self-diffusion, and that this is the reason for the observed proportionality between creep rate and stress.

In order to investigate this problem further, it is necessary to look into the relationship that might be expected to exist between diffusion rates and shear rates. Eyring³ has shown that, given the rate at which a substance diffuses through itself (the rate of self-diffusion) and if the unit molecular process in shear is the same as that in diffusion, it should be possible to calculate a corresponding shear rate or viscosity coefficient. This is readily understood as follows:

The net rate at which molecules move in a given "forward" direction (the diffusion rate) is given by the difference between the total number of molecules that jump in the forward direction in one second, and the number that jump in the opposite direction in the same time. Since the number of molecules that jump through a given plane is proportional to the total number of molecules present that are

* A further indication that microcreep does not occur by the movement of dislocations is found in the remarks (p. 65) to the effect that potential energy curves such as those typical of the movement of dislocations (Fig. 11) tend to give creep rates that depend exponentially on the stress at much lower stresses than would be expected from the hyperbolic sine law. Since flow according to this law is required in order that creep rates can be proportional to shear stresses, it must be suspected that a potential energy curve such as that in Fig. 11, and hence flow by means of dislocations, does not occur in the microcreep of tin.

capable of jumping through this plane, the number jumping forward through a plane having a unit area per second is

$$n_+ = k_0 c \lambda \quad [30]$$

where k_0 is the rate at which a single molecule jumps (number of jumps per second by one molecule), c is the concentration of the molecules behind the plane, and λ is the distance moved by a molecule in one jump (k_0 is the same as n in Eq. 10). $c\lambda$ thus represents the total number of molecules behind the plane that are capable of jumping through it in one leap. Similarly, the number of molecules jumping in the opposite direction is

$$n_- = k_0 \left(c + \frac{dc}{dx} \lambda \right) \lambda \quad [31]$$

where $\frac{dc}{dx}$ is the gradient of the concentration in the forward direction, so that $\left(c + \frac{dc}{dx} \lambda \right)$ is the average concentration of molecules in front of the plane. Then the diffusion rate is given by

$$n_+ - n_- = -k_0 \lambda^2 \frac{dc}{dx} \quad [32]$$

and the ordinary diffusion coefficient Δ is

$$\Delta = k_0 \lambda^2 \quad [33]$$

On the other hand, it has been shown that the shear rate may be given by

$$s = \frac{2\lambda}{L} k_0 \sinh qA\sigma/kT \quad [34]$$

or, substituting Eq. 33,

$$s = \frac{2\Delta}{\lambda L} \sinh qA\sigma/kT \quad [35]$$

If Newtonian flow is involved, $\sinh qA\sigma/kT$ can be replaced by $qA\sigma/kT$ and the viscosity coefficient calculated as

$$\eta = \frac{\sigma}{S} = \frac{\lambda L kT}{2qA\Delta} \quad [36]$$

This equation has been found to hold well

for diffusion processes in ordinary liquids when reasonable values of λ , L , etc., are used; it will now be applied to a calculation of the rate of flow of solid and molten lead.

The rate of self-diffusion of lead (thorium B) into molten lead at 343°C . has been found³² to be 2.2 sq. cm. per day = 2.55×10^{-5} cm. per sec., and the viscosity of lead at 343°C . can be found from a short extrapolation of a logarithmic plot of viscosity data³³ to be $\eta = 0.0266$ poises. Using the observed Δ and taking $q = 1$ and $\lambda = L = 2l = \sqrt{A} = 3.1 \times 10^{-8}$ cm., η is calculated to be 0.107 poises. This is too large by a factor of 4 (not too serious an amount when the uncertainties in λ , L , l , and A are taken into consideration).

Turning to the case of solid lead, let us compare the creep rate of 4×10^{-6} per day at a tensile stress of 200 lb. per sq. in. measured by McKeown²³ at room temperature (300°K .) with that expected from Eq. 35. This corresponds to a shear rate of 3×10^{-6} per day and a maximum shear stress of 100 lb. per sq. in. The diffusion rate of lead into solid lead at 300°K . can be calculated from an extrapolation of the data of Seith³⁴ to be $\Delta = 3.5 \times 10^{-15}$ sq. cm. per day. Taking $q = 1$, $Al = 15\text{\AA}^3$, and $\lambda = L = 3\text{\AA}$., $\sinh qA\sigma/kT = 2.5 \times 10^{-3}$ and a shear rate of 1.9×10^{-2} per day. This is 5000 times *faster* than the rate observed by McKeown, whereas a shear rate calculated for molten lead would be 4 times too *slow*. Furthermore, if the creep of lead were occurring by means of a self-diffusion mechanism under the present conditions of stress and temperature, the conditions leading to ordinary viscous (Newtonian) flow would obtain and the creep rate would be proportional to the applied stress, which was not found to be true by McKeown.*

Therefore, the observed creep of solid lead does not occur by any simple self-

* Evidence for the existence of ordinary viscous flow in lead at low stresses may, however, be found in the data of Hanfstengel and Hanemann³⁶ and of Moore and Betty.³⁷

diffusion mechanism while the flow of molten lead probably does involve such a mechanism; and conversely, either the unit molecular self-diffusion process in solid lead does not involve shear, or self-diffusion in solid lead cannot be the simple, homogeneous process postulated above, but occurs chiefly along preferential paths in the crystal—paths so located with respect to one another that macroscopically observable shear can result from movements along only *at most* one out of every 5000 of the paths in the sample of lead studied by McKeown.

If the microcreep discovered by Chalmers for single crystals of tin also arose from a self-diffusion mechanism proceeding chiefly along certain paths in the crystal, we might be able to understand certain other characteristics of microcreep found by Chalmers. For instance, he found that associated with microcreep there is a rapid strain-hardening, and the total extension obtainable through the action of the microcreep mechanism is more or less independent of the applied stress. On the other hand, the hardening so produced disappears within a few hours, or after a larger stress is applied for a short time. Chalmers explained this by saying that the microcreep is the result of the flow of dislocations already present in the metal, that this number is limited, and that new dislocations form very slowly at such low stresses; therefore, only the amount of creep corresponding to the number already present is possible. In the light of the present theory, however, it seems more likely that the rapid strain-hardening associated with microcreep is caused by the exhaustion of the diffusion paths favorably located for shear. Since self-diffusion occurs because of the presence of empty lattice sites in the crystal, this exhaustion might be due to a depletion of all of the empty sites along the given paths. The regeneration of the crystal on standing would then result from a slow seeping of new empty sites

into the paths from the surrounding medium, while the regeneration due to the application of larger stresses might result from a readjustment that makes new paths of self-diffusion effective in causing shear.

Chalmers found that after a crystal had undergone all of the microcreep of which it is capable there was a small residual creep which proceeded exceedingly slowly and whose rate seemed to be independent of the stress. (This last type of creep was not, however, very thoroughly studied, owing to the experimental difficulties necessarily involved.) Chalmers ascribed this residual creep to the slow formation of new dislocations in the crystal. Such an explanation, however, is clearly inadmissible according to the present theory; the rate of formation of dislocations should be markedly affected by the applied stresses, because, as we have seen, the applied stresses can do a great deal of work to aid in the formation of any dislocation that will ultimately result in shear, and this, by altering the activation energy, alters the rate. Instead, we would suggest that this residual creep is caused by the slow seeping of holes (empty lattice sites) into the effective diffusion paths as mentioned above. Since the direction of this seepage is perpendicular to the shear direction, the applied forces cannot help the holes appreciably in their motion into a path of shear, and the resultant shear rate is independent of these stresses insofar as the rate of seepage of a hole into a path is slow relative to the rate of the diffusion of the hole down the path. (Cf. the over-all rate of two successive chemical reactions.)

CONTRAST WITH OTHER THEORIES

The numerical results of the application of Eq. 18 to actual creep data may be said to tend to verify the theory that metals deform by means of dislocations; on the other hand, any theory based upon ideas of self-diffusion, such as that of Kanter,⁸ does not seem to be valid under most conditions.

creep rate vs. stress plots shows that in general the effect *is* small.

The interpretations of static tensile tests in the light of Becker's dynamical theory made by Orowan⁵ are equally applicable with the present theory, and the value of regarding the problem of the plasticity of metals as essentially one of rates, which was emphasized by these writers, must not be overlooked.

CONCLUSION

If the question be asked, "What structural and chemical features of a material must be sought after in order that the material will creep at the slowest possible rate at a given temperature and under the action of a given stress?" the answer given by Eq. 18 must be that ΔS^* should have as large a negative value as possible, ΔH^* should be as large as possible, and qAl should be kept as small as possible. In the light of the results of our application of this equation to actual creep data, we must admit that the factors that tend to make ΔS^* have a large negative value are as yet only incompletely understood. ΔH^* can be made large by employing a material with a high elastic modulus, or by including in the structure of the material a network of chemical bonds with a strongly directive character instead of the less strongly directive metallic bonds,* or perhaps by the introduction of many dislocations in the manner of Taylor's theory. qAl can be made smaller by introducing more and more "opaque surfaces" or other barriers

preventing the lateral extension of dislocations (i.e., keeping A small).

A fundamental attack on the problem of creep can be made by studying experimentally and in more detail just what factors affect ΔS^* , ΔH^* , and qAl . If these factors were more thoroughly understood, it seems not unlikely that considerable advances could be expected in the development of creep-resisting alloys. Experimental work on creep in metals with a view to a more complete understanding of the applicability of Eq. 18 will begin shortly.

SUMMARY

1. Eyring's general statistical mechanical theory of shear rates has been outlined and applied to available data on the creep of metals.

2. From the values of the constants in Eyring's equation required to fit the data, it is shown to be very likely that metallic creep usually occurs by the shear of rather large blocks of material in the unit molecular process, rather than by the movement of single atoms past one another as in diffusion. This is shown to fit in well with existing ideas on the flow of crystals by means of dislocations.

3. The questions of why some metals are so much softer than others, the effects of impurities on hardness, the softness of single crystals, and the role of self-diffusion in creep are considered in the light of the theory, and it is shown how answers to these questions (and others similar) might be obtained by use of the theory.

4. The relationship between the present theory and previous theories is discussed.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. E. U. Condon for pointing out the applicability of Eqs. 15 and 18 to metallic creep and for making available his own unpublished work on the problem; and to Prof. F. Seitz, Dr. A. Nadai and Dr. T. A. Read for helpful discussions.

* This effect of directive bonds is probably responsible for the great resistance to creep shown by diamond, quartz, and many of the silicates on the one hand (all of these having strongly directive bonds), and for the very slight creep resistance of metallic sodium (which has a typically metallic bond). It may also be responsible for the greater hardness of steels over pure iron, the bonds in Fe_3C being probably much more nearly homopolar than those in pure iron, and hence more strongly directed.

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KEY TO NOTATION

- s = shear rate.
 λ = distance in shear direction moved by flow units relative to one another in the unit process. See Fig. 2.
 L = distance between layers of units of flow. See Fig. 2.
 ν = net number jumps per second of unit of flow in shear direction.
 E = energy.

- ΔH^* = energy of activation per mol.
 ΔS^* = entropy of activation per mol.
 ΔF^* = free energy of activation per mol.
 k = Boltzmann's constant = 1.38×10^{-16} erg per molecule per degree C.
 h = Planck's constant = 6.626×10^{-27} erg-second.
 R = gas constant = 1.986 cal per mol per degree C.
 T = absolute temperature.
 A = area of unit of flow in the shear plane (area on which the shear force acts).
 N = Avogadro's number.
 S = entropy.
 M = Nm = molecular weight.
 l = distance through which the shear stress acts in carrying the unit of flow from the normal to the activated state.
 f = shear stress acting on a unit of flow.
 σ = macroscopically observed shear stress.
 q = stress concentration factor = f/σ .
 d = length of a dislocation.
 η = coefficient of viscosity = σ/s .
 e = energy of a molecule.
 m = mass of molecule.
 g = acceleration of gravity

DISCUSSION

(J. J. Kanter presiding)

S. DUSHMAN,* Schenectady, N. Y.—Independently of Dr. Kauzmann, I had deduced from Eyring's theory an equation for creep that is in formal agreement with that derived in this paper in Eqs. 15 and 18. In view of the fact that the factor $(\lambda/L)(kT/h)$ in the latter has the dimensions of a frequency, the assumption has been introduced that this frequency is determined by the Debye specific heat frequency, which in iron, nickel and cobalt has the approximate value 8×10^{12} . Inserting this value into Eq. 18, it is thus possible to determine the free energy as a function of stress. Assuming, furthermore, that the change in entropy is zero, these considerations lead to a relation for creep of the form

$$\log S = \log \nu_0 - \frac{Q_0 - J\alpha f}{4.578T} \quad [37]$$

where the log is taken to base 10, ν_0 is the Debye frequency, α is a constant which has the dimensions of a volume, f is the stress expressed in dynes per sq. cm., J is the reciprocal of the mechanical equivalent of heat; Q_0 is expressed in terms of calories per gram-atom, and T is the absolute temperature in

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degrees Kelvin. Of course the creep rate must be expressed in terms of reciprocal seconds.

In order to test the validity of this equation, an experimental technique has been used that may be described briefly as follows: The materials, such as 18-8, or other alloy, is drawn down to a wire of 10-mil diameter, and made up into V-shaped filaments 15 cm. long per leg of the V. This is inserted in a bottle through which purified nitrogen is passed slowly, and the weight is suspended from the bottom of the V. For the cross section of the wire used, a weight of 1 gram corresponds to a stress of 14 lb. per sq. in. The filament is heated by passing current through it and is maintained at the desired temperature by comparing the brightness with that of a calibrated gas-filled tungsten lamp of the movie-projector type. Before the test of creep rate the filaments are annealed at a high temperature, without stress.

While the results of the first experiments (on 18 Cr, 8 Ni alloys) seemed to be in agreement with the assumption of zero entropy change, and this result was reported at the time of the presentation of this paper, subsequent results have shown the necessity for introducing a finite entropy term, as has been done by Dr. Kauzmann. The magnitude of ΔS^* varies from about -9 cal. per deg. per mol for 18-8 to about -56 cal. per deg. per mol for platinum. The corresponding values of α and Q_0 for platinum are 75 and 44,000 cal. per gram-atom, respectively; while for 18-8 these values are 31 and 97,000, respectively.

The values of α obtained in these experiments are considerably greater than the atomic volumes, the ratio ranging from 100 to 300. This may be due to a stress-concentration or the presence of atomic "domains" which move as units. The latter suggestion has also been made by Dr. Kauzmann.

A more detailed discussion of the results obtained for a number of metals and alloys will be published in the near future.

J. J. KANTER,* Chicago, Ill.—It is gratifying to see the publication of a paper that seriously attempts to interpret creep phenomena from the viewpoint of physics and chemistry. The engineering application of creep data has encompassed little more analysis of creep and

flow phenomena than the calculation of empirical expressions useful in problems of applied mechanics. From the metallurgical point of view, however, more fundamental analyses of creep and flow will unquestionably prove of practical importance. Dr. Kauzmann's method of analysis affords a new approach toward this interpretation and merits thoughtful consideration and study. It is to be hoped that experiments will be initiated specifically planned to test out the hypotheses of Kauzmann's analysis.

There is one question with regard to the activation energies shown in Table 1. Values are shown derived from creep tests for seven different ferritic steels ranging from 17,000 to 102,000 cal. per gram mol. There is no very basic metallurgical difference among materials; they might have various grain sizes and other structural differences, but all these steels are composed of essentially the same type of ferrite crystals. It would not seem that a variation of stress concentration factor could be present among the steel to so widely vary the activation energy associated with slip. My question is in regard to the explanation of this wide divergence in the activation energies calculated according to Dr. Kauzmann's method upon similar materials. Does he regard the data used as so highly uncertain, or does this 600 per cent range of activation energy value represent an actual metallurgical variation in the material?

Another aspect of creep on which Dr. Kauzmann's interpretation would be of interest is the fact that such tremendously different creep rates are observed in a given material when its grain size is altered either through working or heat-treatment. The implications of Dr. Kauzmann's method of analysis should be studied in regard to such effects.

T. A. READ,* East Pittsburgh, Pa.—In comparing creep data with Eq. 25, the author assumes that the dependence of the creep rate on stress at constant temperature is given entirely by the coefficient $\exp(qA/r/2KT)$. The success of this assumption is somewhat surprising in the case of data on steady-state creep. One might expect the parameters ΔS^* and ΔH^* to depend on the stress, inasmuch as

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they must be structure-sensitive properties. The structure of the metal presumably will be affected by prolonged loading, particularly at the higher stress levels.

W. KAUZMANN (author's reply).—It is interesting that apparent confirmation of the general features of creep as given here has been found by Dr. Dushman in his experiments, and the publication of his complete results is awaited with interest. It should be strongly emphasized, though, that owing to the frequent dependence of qAl , or α , on the temperature, reliable activation energies usually cannot be obtained from the temperature coefficient of the creep rate at constant stress. Indeed, this temperature sensitivity of the size of the unit of flow seems to be one of the outstanding characteristics of the whole phenomenon of creep and demands a prominent position in any attempt at understanding creep.

If the size of the unit of flow changes with temperature, the activation energy for their flow probably also changes with the temperature, and this bears strongly on Dr. Kanter's first point. If this temperature variation does occur, the method of obtaining the activation energies of Table 1 will not be valid. Therefore, as was pointed out in the paper, neither these values nor the entropies given in the table probably have physical significance as they stand. But if we are willing to say that the entropy of activation is zero (and this may not be far from the truth), the activation energy will be identical with the free energy of activation, ΔF^* at any given temperature. A glance at Table 1 will show that 1000°K.

(= 1300°F., which is only a little higher than the temperature for which most of the data on the steels were obtained) the values of ΔF^* for the steels are not very different and that, therefore, the true activation energies do not vary as markedly as Table 1 would indicate.

It would not be altogether unreasonable, however, if there were a wide difference in the activation energies for creep between different steels: we must remember that there is every indication that *structure* as well as *composition* plays an important role in the plastic properties of metals, so that we must expect other factors beside the chemical composition to have their effect on the activation energy.

The effects of grain size, heat-treatment, and cold-working on the creep rate from the standpoint of the theory are now being investigated experimentally. These effects undoubtedly are complex, possibly involving simultaneous changes in ΔS^* , ΔH^* and qAl .

Read suggests that by the time a metal has settled down to a steady creep rate at one stress, it might not have the same structure as when it is in the steady state corresponding to another stress, so that most of the data used here in applying the theory are not amenable to such an analysis. While it is important to keep this possibility in mind in evaluating the results of the analyses, the general validity of the exponential creep law for metals must lead us to conclude that things are really not so complicated. Besides, it is not too surprising that the stress, appearing here as it does in an exponent, should operate on the creep rate chiefly through this exponential function rather than indirectly through a second order effect on one of the other terms.

Deformation and Recrystallization of Copper and Brass—Hardness Microstructure and Texture Changes

By R. M. BRICK,* MEMBER, AND M. A. WILLIAMSON,† STUDENT ASSOCIATE A.I.M.E.

(New York Meeting, February 1941)

CERTAIN features of the response of copper and brass to deformation and recrystallization remain obscure. The textures obtained on rolled sheet are listed by Schmid and Boas¹ as:

| Metal | Rolled | Recrys- tallized |
|-------------|----------------------------------|---------------------|
| Copper..... | { 1. (110)[112] 2. (112)[111] | (100)[100] |
| Brass..... | (110)[112] | (113)[112] |

No adequate explanation has been advanced for the presence of the secondary deformation texture of copper and its absence in brass or for the origin of the cubic recrystallization texture of copper.² A recent publication³ attempted to rationalize the above empirically described annealing texture of brass on the basis of retention of the (110) [112] rolling orientation plus twinning about the central octahedral poles of the usual secondary (110) [115] orientation. The difference in the textures of annealed copper as compared to 70-30 brass is also shown by the difference in the position of ears for drawn copper, at 0° and 90°, as compared with drawn brasses, at 45°, for all compositions between 90-10 and 70-30.⁴ Data on indi-

vidual crystals are as yet too few to permit of an analysis of these textures comparable to that of mild steel as made by Barrett and Levenson.⁵

EXPERIMENTAL METHODS

The materials studied included copper specimens cut from the central, equiaxed crystal portion of a tough-pitch wirebar; brass made from this copper and high-purity (99.99 per cent) zinc including alloys of 7 per cent, 15 per cent, 24 per cent, 29 per cent and 36 per cent Zn and large single crystals of 70-30 brass. Sections $\frac{1}{4}$ in. thick of the cast polycrystalline copper and brasses were reduced 40 per cent by rolling, recrystallized to a common grain size of 0.045 mm. and then rolled directly to foil 0.002 in. thick. Hardness readings employing both the Vickers and Rockwell machines were taken at intervals during the reduction. For comparison, similar specimens were cross-rolled—i.e., turned through 90° for each pass—and comparable hardness data were secured. Finally sections from the single crystals of brass were cut to obtain the following initial orientations; these sections were rolled, hardness data secured and a complete micrographic record of structural changes obtained.

| Crystal | A | B | C | D |
|------------------------|-------|-------|-------|-------|
| Rolling plane..... | (100) | (100) | (110) | (110) |
| Rolling direction..... | [100] | [110] | [115] | [111] |

A part of the work described in this paper has been presented in the form of a thesis by Merritt A. Williamson in partial fulfillment of the requirements for the degree of Master of Science at Yale University. Manuscript received at the office of the Institute Nov. 25, 1940. Issued as T.P. 1299 in METALS TECHNOLOGY, February 1941.

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¹ References are listed at the end of the paper.

| Crystal | F ^a | G | H ^a | I |
|------------------------|----------------|-------|----------------|-------|
| Rolling plane..... | (112) | (112) | (111) | (111) |
| Rolling direction..... | [111] | [110] | [112] | [110] |

^a Textures were determined for these specimens at 80 and 99 per cent reductions. All pole figures⁴ were derived from X-ray photographs of 0.002-in. sheet taken at 10° intervals of rotation about longitudinal and transverse axes.

STRAIGHT AND CROSS-ROLLED COPPER

Averages of the work-hardening curves of six different copper specimens are reproduced in Fig. 1*a*. At all reductions between 30 and 90 per cent, the straight-rolled copper showed a distinctly higher hardness than the cross-rolled copper, amounting to a maximum of 7 points on the Rockwell B scale. The difference was reproduced under varied rolling techniques employing 4-in. laboratory rolls but was not found when a large slab was reduced, in fewer passes, in a commercial mill employing large (18-in.) rolls.

The straight-rolled copper had an orientation (Fig. 2*a*) similar to that shown by Göler and Sachs² with one important exception, the as-rolled (99 per cent) sheet in addition to the usual (110) [112] texture and the secondary (112) [111] texture showed distinct evidence of material in the (100) [100] position. This is significant in view of the recrystallization texture (Fig. 2*b*) which, in agreement with other workers, was almost entirely in the cubic position; indeed the X-ray photographs appeared to show almost a single-crystal orientation. Thus copper conforms to many other cubic metals—e.g., the Fe-Ni alloy studied by Sachs and Spretnak⁶—inasmuch as a minor part of the deformation texture may become the chief or sole recrystallization orientation. This appears to be a more logical explanation of the cubic recrystallization texture of copper than that offered by Cook and Richards⁷ who suggest that the four central octahedral poles of the (110) [112] worked texture maintain their identity but adjust their positions. Such

an adjustment would require rotations in mutually irreconcilable directions.

The cross-rolled copper (Fig. 3*a*), rather than showing three disparate orientations in the worked structure, appeared to be primarily in a (110) [223] texture, with other strong areas most readily explained on the basis of twinning about central (111) poles of the (110) [223] orientation. This cannot be construed as direct proof of mechanical twinning, which Mathewson and Van Horn⁸ were not able to cause in copper. It is evidence that is suggestive of twinning, particularly in view of the lower hardness of the cross-rolled material. Twinning may be considered as an internal reorientation process tending to relieve crystallographic distortion, an indubitable source of hardness. Further support for this hypothesis is offered by the fact that the cross-rolled copper was found to have a slightly higher recrystallization temperature (Fig. 1*b*) at 30 per cent, 50 per cent and 70 per cent reduction intervals (thus showing less internal distortion) and that for these specific specimens, 99 per cent reduction and $\frac{1}{2}$ hr. at 400°C. anneal, it showed a considerably coarser grain than the straight-rolled material. A complicated recrystallization texture was found and is explained in the pole figure (Fig. 3*b*) as derived from the worked texture (110) [223], twins from this and from the weak (110) [112] deformation structure and also the usual (100) [100] copper recrystallization texture.

POLYCRYSTALLINE BRASSES, 7 TO 36 PER CENT ZINC

The work-hardening capacity of solid solutions with varying solute content are part of a separate line of work and will not be reproduced here. However, in contrast to copper, no distinct and regular difference was found between straight-rolled and cross-rolled brasses of the same zinc content. The textures of all these normally rolled brasses was the same as that previ-

ously reported for the 70-30 brass.³ The deformation orientations were (110) [112] with a secondary spread (110) [113] - [117]. The recrystallization textures obtained

stresses of the cut, polished and etched faces. Furthermore, the Vickers impressions all showed long and short axes as well as convex or concave edges as a result of

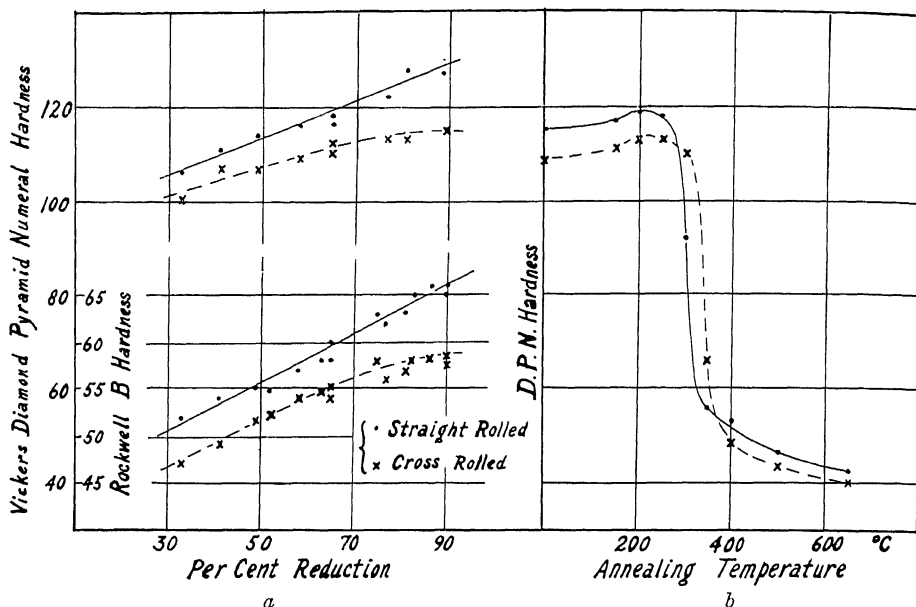


FIG. 1.—WORK-HARDENING AND TYPICAL ANNEALING CURVES FOR STRAIGHT AND CROSS-ROLLED COPPER.

b. 50 per cent reduction, $\frac{1}{2}$ -hour cumulative anneals.

could again be empirically described as (113) [112] or more rationally as partly reproduction of the primary deformation texture plus twins from central octahedral poles of the secondary deformation orientation. The origin of the marked difference between textures and, relatedly, earing characteristics, of copper and brass has been located by Dahl⁹ at between 1 and 5 per cent Zn content, while considerably earlier work by Bauer, v. Göler and Sachs¹⁰ has shown that the transition in behavior occurs for alloys containing 1.8 per cent Zn.

SINGLE CRYSTALS OF 70-30 BRASS

Hardness values on the different crystal faces of these undeformed specimens were somewhat variable because of slightly different densities and the impossibility of assuring equal freedom from machining

elastic and plastic anisotropy. Average readings gave relative hardness in the following decreasing order; (111), (110), (112) and (100), (221).

The relative work-hardening rates are reproduced in Fig. 4. It appears that hardening takes place at a different rate and to a different degree as a function of the initial orientation, thus confirming previous studies performed at Hammond Laboratory.¹¹ Further work is required before these different rates can be directly related to crystal rotation as a unit or fragmentation with individual rotations into textural positions.¹²

Microscopic examination of the structural alterations during rolling included taking a large number of photomicrographs, most of which need not be reproduced here.¹³ Certain generalizations may be

stated on the basis of this evidence as follows:

1. As in polycrystalline brass, no deformation markings appeared until reductions exceeded 20 per cent.

become transverse to the rolling direction. At this same reduction, the gross orientation has generally been found to start changing from essentially single positions to textural spreads, which in most cases

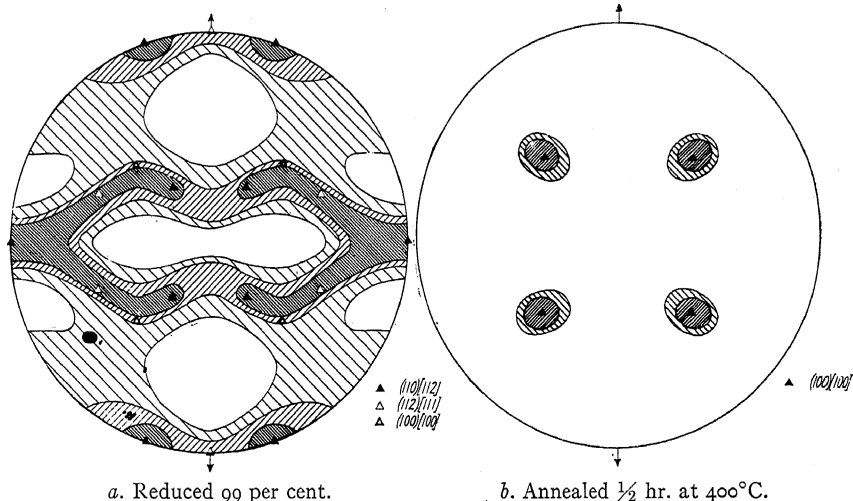


FIG. 2.—OCTAHEDRAL POLE FIGURES FOR STRAIGHT-ROLLED COPPER.

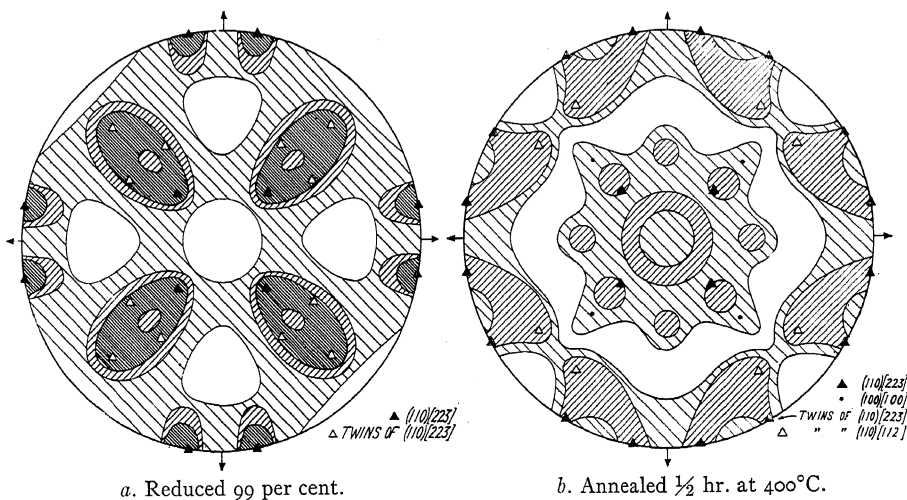


FIG. 3.—OCTAHEDRAL POLE FIGURES FOR CROSS-ROLLED COPPER.

2. At low reductions, 20 to 40 per cent, the markings could be directly identified as occupying octahedral planes of the matrix.

3. At higher reductions, about 70 per cent, the deformation lines appeared wavy, broken up, branched but tending to

could account for the markings as (111) traces, but without definite assurance.

One noteworthy exception to this vague identification at higher reductions was crystal H , rolled on a (111) plane in a $[112]$ direction. At an 80 per cent reduction, it showed essentially a single $(110)[100]$

orientation (Fig. 5*a*), previously shown to be a fairly stable position up to reductions exceeding 90 per cent. Fig. 5*b* contains some straight-line markings whose direc-

octahedral poles. It is significant in this connection to refer to Fig. 4*d*, which shows that this crystal did not harden, in fact softened, while being rolled from 50 to

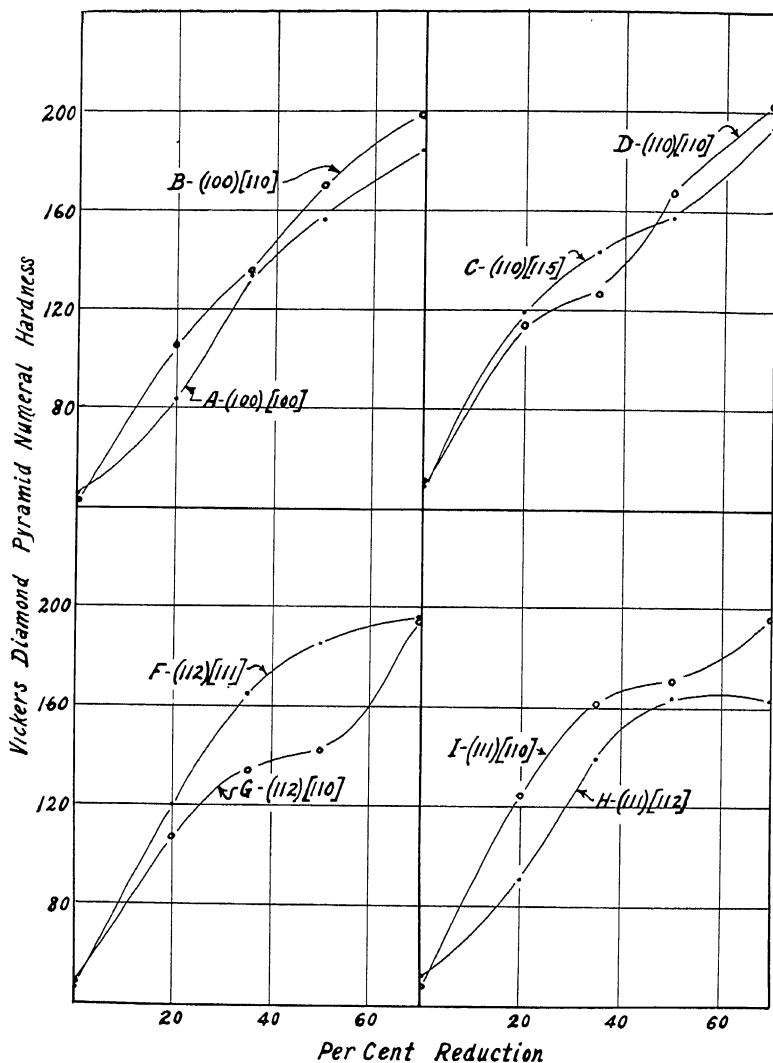


FIG. 4.—WORK-HARDENING CURVES FOR SINGLE CRYSTALS OF BRASS ROLLED FROM INDICATED INITIAL ORIENTATIONS.

tions correspond to positions of the peripheral octahedral poles. A transverse photomicrograph confirmed this identification of the markings as being traces of

70 per cent total reduction. Fig. 5*c* shows the shift to a nearly symmetrical normal deformation texture (110) [112] after 99 per cent reduction. The recrystallization tex

ture, not reproduced here, again appeared to be derived from the worked structure directly or by twinning.

One other rolled single crystal in the

banded structure than Fig. 5*b*. The recrystallization texture, Fig. 6*b*, showed six moderately strong peripheral (111) areas, apparently directly derived from the

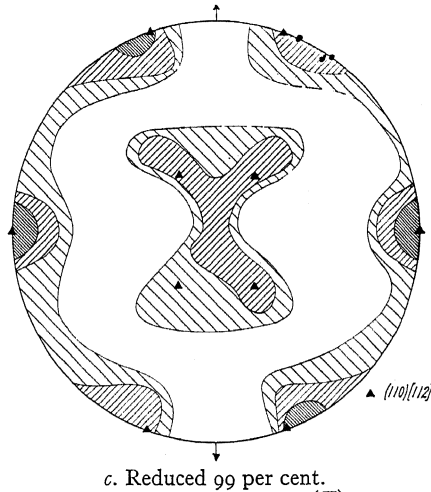
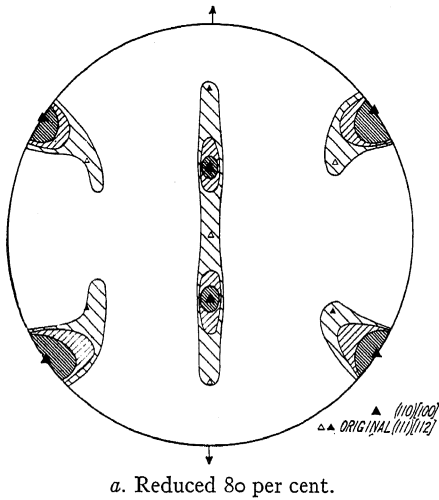


FIG. 5.—OCTAHEDRAL POLE FIGURES OF SINGLE CRYSTAL (*H*) OF BRASS ROLLED FROM AN INITIAL (111)[112] ORIENTATION.

initial orientation (112) [111], was studied on the basis of its deformation and recrystallization textures. After a reduction of 80 per cent, the material was still near its original orientation but, in addition, had developed in equal intensity a complete mirror image of this (Fig. 6*a*) corresponding to a much heavier and also less well defined

deformation texture. It is interesting that this conformation has been found in commercial brass with the corresponding development of six ears on drawn cups.* The same crystal after a 99 per cent reduction (Fig. 6*c*) again approached the normal rolled texture (110) [112] and the texture of

* Private communication; Dr. H. L. Burghoff.

the recrystallized specimens Fig. 6*d* approached the normal annealing orientation, empirically $(113) [112]$. It is particularly evident that areas marked *A* in Fig. 6*d*

SUMMARY

Copper cold-rolled in one direction work-hardened more than comparable cross-

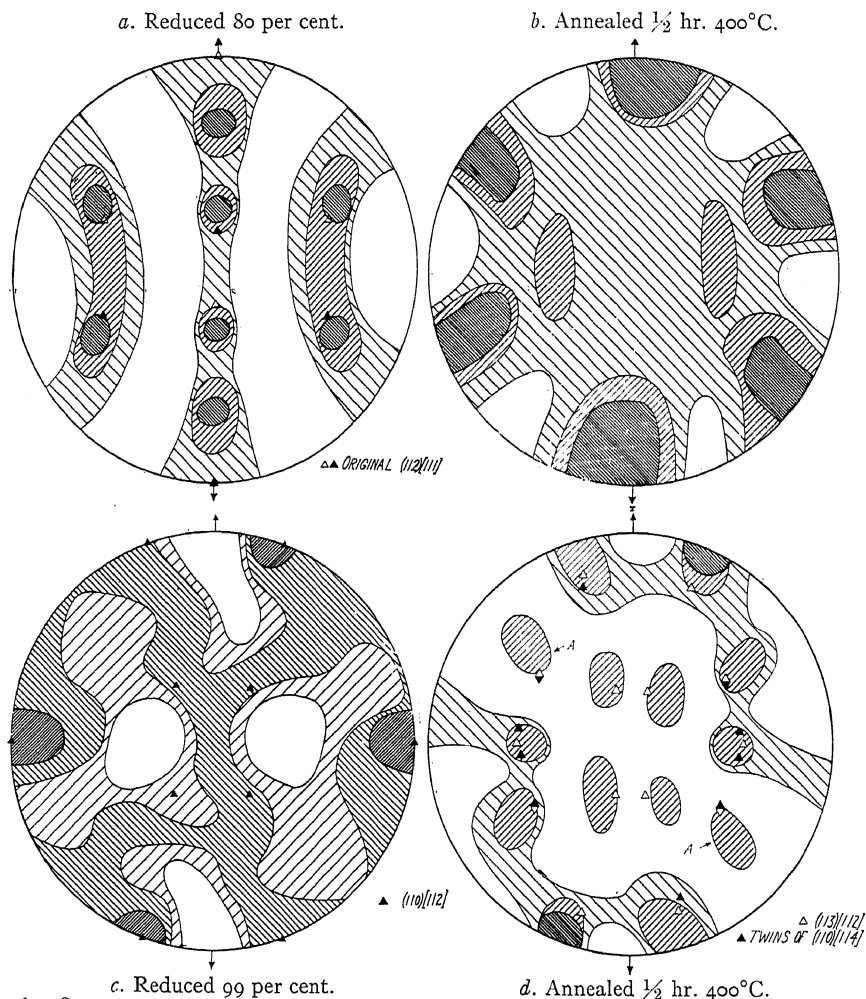


FIG. 6.—OCTAHEDRAL POLE FIGURES OF SINGLE CRYSTAL (*F*) OF BRASS ROLLED FROM AN INITIAL $(112)[111]$ ORIENTATION.

cannot be readily attributed to reproduction of the rolling texture but do conform to the empirical $(113) [112]$ orientation or to twins of the rolled structure. It appears to be significant in view of the fact that this specimen had a work-hardening curve (Fig. 4*c*) more like that of polycrystalline brass than any of the other single crystals.

rolled metal. The straight-rolled material had a texture similar to that described in the literature, both $(110) [112]$ and $(112) [111]$ structures being present and in addition some material in the hitherto unreported $(100) [100]$ orientation. The latter is significant since it constitutes the known recrystallization texture, which in this case

was so sharp that the material appeared to be nearly a single crystal. The recrystallization process thus appears to consist primarily of the growth of stable (100) [100] nuclei at the expense of the dominant but less stable other orientations.

The lower hardening of the cross-rolled copper may plausibly be attributed to mechanical twinning acting to relieve internal distortion since the texture of this sheet was best explained by a (110) [223] orientation plus twins from the central octahedral poles of the texture. This hypothesis is also consistent with the observed higher recrystallization temperature and coarser grain of the cross-rolled material. The recrystallization texture was in this case very complicated but apparently consisted of the original orientations in somewhat shifted relative intensities.

Polycrystalline alpha brasses of from 7 to 36 per cent Zn were quite different from copper and corresponded, texturally, to the 70-30 brass previously reported.

Several single crystals of brass were rolled and the accompanying changes in their hardness, microstructures and in two cases, textures, were determined. The data were in conformity with previous work in showing that deformation markings at low reductions were along octahedral planes. In one specimen rolled to a 70 per cent reduction, the pole figure rather definitely indicated its deformation lines occurred along (111) planes and thus could be mechanical twins. This same specimen significantly failed to work-harden on being rolled from 50 to 70 per cent reduction. The end deformation textures again approached the normal (110) [112] structure although other relatively stable orientations appeared to persist beyond an 80 per cent reduction. The symmetric or nonsymmetric recrystallization textures could best be rationalized on the basis of retention of original orientations or twins therefrom.

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DISCUSSION

(J. T. Norton presiding)

C. S. BARRETT,* Pittsburgh, Pa.—An extensive study of the textures in rolled copper and brass has been made by two Russians,¹⁴ and should be considered in connection with these results. Pole figures for (111), (200) and (220) planes were accounted for by them as the sum of the "ideal orientations" shown in Table 1.

TABLE 1.—*Ideal Orientations of Iweronowa and Schdanow*

| Orientation No. | R.P. | R.D. | Copper | Intensity | |
|-----------------|-------|-------|--------|-------------------------|---------------------------------------|
| | | | | Brass, 95 to 5 Per Cent | Brass, 80 to 20 and 62 to 28 Per Cent |
| 1 | (110) | [112] | S | S | S |
| 2 | (112) | [111] | S | | |
| 3 | (124) | [335] | M | W | W |
| 4 | (110) | [100] | W | M | S |
| 5 | (100) | [100] | W | | |

In straight-rolled copper they found all five orientations with the relative intensities (strong, medium, and weak) listed in the table; in the brasses ranging from 5 to 28 per cent Zn,

* Metals Research Laboratory, Carnegie Institute of Technology.

¹⁴ W. Iweronowa and G. Schdanow: *Walztexur des Alpha-Messings. Tech. Phys. U.S.S.R.* (1934) **1**, 64.

the intensities were altered as shown, and some components disappeared (Nos. 2 and 5). Schmid and Boas found the first two ideal textures in copper, the first one only in brass; Sachs and Spretnak found Nos. 1, 2 and 5 in Fe-36 per cent Ni. Fig. 2*a* herein, for straight rolled copper, is interpreted in terms of Nos. 1, 2 and 5, but 3 and 4 also fall within the shaded areas of the pole figure, just as in the very similar texture found by the Russians.

It is always recognized that the details of the pole figures are not fully described by one or two ideal textures, and even with this list of five there are still significant details that are not indicated. There is the interesting fact, for instance, that in rolled brass there is considerable material with (111) in the rolling plane, while there is none in copper. Figs. 5*a*, 5*c*, 6*a* and 6*c* are in accord with this behavior of brass, for all show material at the center of the (111) pole figure. That the list is not complete is suggested by reference to Dr. Brick's paper (ref. 3) on rolled brass, and also by some tests made at the Metals Research Laboratory on copper crystals reduced 96 per cent by rolling, which have taken orientations other than any on this list, yet lying within the dense areas of the polycrystalline pole figure. Probably, also, there are orientations in the list that are not stable at high reductions. Crystal H arrived at orientation No. 4 after 80 per cent reduction, but gave it up in favor of No. 1 with further rolling. We have rolled some crystals of copper and have had multiple orientations form from a crystal in orientation No. 2.

I should like to add a word about the role of twinning. There are 20 different twins of the five textures listed above; allowing for those that are similarly related to the rolling direction and rolling plane there are still, I believe, 13. These, together with the five orientations listed, give a total of 18. Very few orientations

can be found that do not lie near one of these 18; consequently, it is difficult to test a twinning theory by an investigation of the polycrystalline pole figure for twinning relationships within it. There are other difficulties also: a plane of symmetry of the rolling process may also be a twinning plane for one of the ideal textures. This is true of orientation No. 1 and weakens some of the conclusions about twinning in the paper by Cook and Richards (ref. 7).

We are rolling some copper crystals in an attempt to get more definite tests of the twinning theory and a better general understanding of the origin of the polycrystalline texture; thus far multiple orientations have developed in several crystals, but orientations that are twins of each other have not been found.

R. M. BRICK (author's reply).—We are grateful to Dr. Barrett for calling our attention to the work by the Russian authors. The comparisons and interpretative statements made by Dr. Barrett are in accord with our ideas and require no further comment.

In regard to the twinning mechanism, it must be conceded, of course, that the pole figure of a severely deformed metal cannot prove that the twinning mechanism is operative or even demonstrate with certainty that twinned orientations are present. On the other hand, the pole figure of the cross-rolled copper fits in very nicely with the twinning hypothesis and, as Mr. Williamson pointed out in the presentation, we believe that a lesser work hardness would accompany twinning. Since it cannot be proved by the pole-figure method, the matter must remain at its present status. Perhaps other methods of attack will be more successful in demonstrating whether deformation markings in copper and brass are twinning, and if they are not, what is their function in the rolling and crystallization processes.

Corrosion of Copper and Alpha Brass—Film-structure Studies

By J. H. HOLLOMON,* STUDENT ASSOCIATE, AND JOHN WULFF,† MEMBER A.I.M.E.

(New York Meeting, February 1941)

SERVICE failures in brass condenser tubes are often due to corrosion. One of the commonest types of corrosion reveals a surface structure of redeposited copper.¹ The study of the effect of alloy addition agents in preventing this kind of corrosion has received impetus from the extensive publication of Bengough and May.² The mechanism of such inhibition gauged from immersion corrosion,² cell corrosion,³ and electrolytic potential⁴ measurements is controversial. This controversy may be attributed in part to a lack of definite knowledge⁵ of the actual nature of the initial films formed in corrosion experiments. In our own corrosion work on copper and 70-30 brass this lack became apparent and necessitated an examination of surface films by X-ray and electron diffraction methods. The present paper is but an introduction to the subject of inhibition and reports the structure of films formed in active corrodents.

EXPERIMENTAL PROCEDURE

The arsenical coppers and brasses used in this investigation were made by one of the writers* in the plant of the Revere Copper and Brass Co. at Rome, N. Y. Standard commercial melting practice was followed. O.F.H.C. copper and electrolytic zinc were used and all arsenic additions were made by additions of a master copper

alloy. The final analyses are given in Table I. Likewise, the extrusion, cold-rolling, and intermediate anneals employed followed standard usage. Final heat-treatments were given to all materials to produce a similar grain size (0.035 to 0.045 mm. for brass and 0.015 to 0.025 for

TABLE I.—Analyses of Arsenical Brass and Copper Employed

| No. | As, Per Cent | Cu (O.F.H.C.), Per Cent | Zn (by Dif- ference), Per Cent |
|-----|-----------------|----------------------------|--------------------------------------|
| 1 | nil | 69.46 | 30.54 |
| 2 | 0.014 | 69.40 | 30.59— |
| 3 | 0.024 | 69.66 | 30.32— |
| 4 | 0.031 | 69.42 | 30.55 |
| 5 | 0.045 | 69.70 | 30.25 |
| 6 | 0.087 | 69.51 | 30.40 |
| 7 | 0.256 | 69.74 | 30.00 |
| 8 | 0.425 | 69.51 | 30.07 |
| 9 | 0.70 | 70.00 | 30.— |
| C1 | nil | remainder O.F.H.C. | |
| C2 | 0.013 | | |
| C3 | 0.023 | | |
| C4 | 0.040 | | |
| C5 | 0.084 | | |
| C6 | 0.206 | | |
| C7 | 0.413 | | |
| C8 | 0.603 | | |

copper) for the alloys containing various percentages of arsenic. Samples $\frac{1}{2}$ by $\frac{1}{2}$ by $\frac{1}{4}$ in. were cut from sheet material resurfaced and finished with 0000 metallographic papers. The surfaces were all degreased in alcohol and benzine before immersion. After immersion in the corrodent, they were washed gently in tap water, dipped first in alcohol and then in pure benzine and allowed to dry in the diffraction apparatus.

The reflection electron diffraction apparatus used has been described by Burwell and Wulff.⁶ Fig. 1 is typical of the photographs obtained. The X-ray apparatus was

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¹ References are at the end of the paper.

of standard powder type employing Phragmén cameras. After insertion of the sample in the electron diffraction chamber, about 30 min. was required to evacuate the

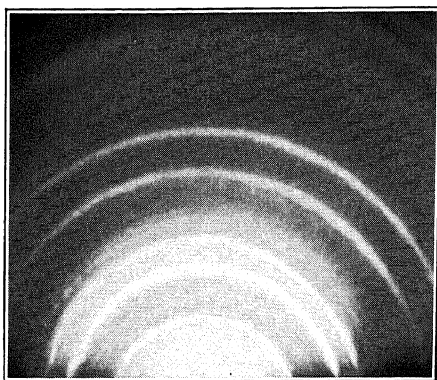


FIG. 1.—ELECTRON DIFFRACTION PATTERN OF O.F.H.C. COPPER CONTAINING 0.084 ARSENIC AFTER 40 MINUTES IN 2N HNO₃.

This pattern consists of rings of As₂O₃ and copper.

chamber, and an exposure of 1 min. to a 30-kv. electron beam to procure a diffraction photograph. The utility of the electron

diffraction method for film studies has been pointed out sufficiently elsewhere;⁷ it permits, in most cases, the study of films less than 100 Å. thick, whereas nearly all X-ray diffraction beams penetrate too deeply into the substrate to be of value in studying very thin films. The results are given in Table 2.

Nonarsenical coarse-grained 70-30 brass, when finished with 0000 paper and thoroughly degreased, gives a pattern representative of cold-worked alpha brass. The cold-working effects are due to surface finishing, since the bulk material is coarse-grained. After being etched to a depth of about 5000 Å., a spotted pattern characteristic of the coarse-grained brass results. Specimens of nonarsenical brass when immersed in a 100-c.c. solution of 5N HNO₃ for 1 hr. give a pattern of copper oxide (CuO) and coarse-grained brass. The CuO film is not visible to the eye for such short periods of immersion, although the grain structure of the basis material is microscopically apparent. When the sample con-

TABLE 2.—Results of Electron Diffraction and Examination of Corrosion Films of Arsenical Brasses and Coppers
Analyses of alloy content of samples given in Table 1

| Pattern No. | Sample No. | Corrodent (Volume = 100 C.C.) in Open Beaker | Time of Immersion | Surface Film | Remarks |
|-------------|------------|---|-------------------|---|---------------------------------------|
| 1 | 1 | 5N HNO ₃ | 1 hr. | CuO + Br | Film not visible |
| 2 | 4 | 5N HNO ₃ | 1 min. | CuO + As ₂ O ₃ + Br | Very thin |
| 3 | 4 | 5N HNO ₃ | 30 min. | As ₂ O ₃ | Very thick |
| 4 | 6 | 5N HNO ₃ | 2 min. | CuO + As ₂ O ₃ + Br | Very thin |
| 5 | 6 | 5N HNO ₃ | 48 hr. | As ₂ O ₃ | Very thick |
| 6 | 9 | 2N HNO ₃ | 10 min. | Sb | Thin |
| 7 | C1 | 5N HNO ₃ | 1 hr. | Cu + CuO | Not visible |
| 8 | C4 | 2N HNO ₃ | 20 min. | As ₂ O ₃ + Cu | Coarse As ₂ O ₃ |
| 9 | C5 | 2N HNO ₃ | 20 min. | As ₂ O ₃ + Cu | Coarse As ₂ O ₃ |
| 10 | C6 | 2N HNO ₃ | 20 min. | As ₂ O ₃ + Cu | Coarse As ₂ O ₃ |
| 11 | 1 | 2N HCl | 6 hr. | Brass ^a | |
| 12 | 1 | 2N HCl | 5 days | Cu or brass ^a | |
| 13 | 3 | 2N HCl | 5 days | Cu or brass ^a | |
| 14 | 4 | 2N HCl | 3 days | Cu + As ₂ O ₃ | Thin |
| 15 | 6 | 5N HCl | 2 hr. | Cu + As ₂ O ₃ | Thin |
| 16 | 1 | 1 gram As ₂ O ₃ in 500 c.c. HCl(6N) | 1 hr. | As ₂ O ₃ ^b | Metallic crystals |
| 17 | 9 | 2N HCl | 10 min. | Sb | |
| 18 | C6 | 2N HCl | 1 day | Cu + As ₂ O ₃ | Thin |
| 19 | C7 | 2N HCl | 1 day | Cu + As ₂ O ₃ | Thin |
| 20 | C4 | 2N HCl | 6 days | CuCl | Precipitate |
| 21 | C4 | 2N HCl | 6 days | As ₂ O ₃ + CuCl | No. 20 scraped |

^a In electron diffraction work it is extremely difficult to distinguish between fine-grained alpha brass and fine-grained copper, because of the slight effect of zinc on the lattice parameter. Nevertheless, coarse-grained alpha brass can be distinguished from fine-grained alpha brass or copper. When grain boundaries are microscopically visible, it is reasonable to assume that all the fine-grained brass arising from the cold-work of surface finishing has been removed and any fine-grained diffraction pattern obtained may then be attributed to copper.

^b Auxiliary X-ray patterns show that the deposit contains metallic arsenic.

tains more than 0.03 per cent As, it is possible in 1 min. in 3 to 6N HNO_3 to procure a film that is just discernible, and whose diffraction pattern is that of copper oxide plus arsenious oxide ($\text{CuO} + \text{As}_2\text{O}_3$), and coarse grained alpha brass. If the time of immersion in the same medium is increased, the film becomes visible to the eye. For a sample containing 0.045 per cent As immersed in 5N HNO_3 for 30 min., the top 100 Å. of the film are essentially arsenious oxide (As_2O_3). Furthermore, the As_2O_3 formed in this length of time is much coarser grained than is the initial arsenious oxide film. Thick films of this kind are not very tenacious and when rubbed off leave an adherent bare film of $\text{CuO} + \text{As}_2\text{O}_3$. Nonarsenical copper immersed in 5N HNO_3 for 1 hr. does not form a film visible to the eye, yet the electron diffraction pictures reveal a copper oxide coating. When arsenic in amounts greater than 0.04 per cent is present in copper, the film consists essentially of As_2O_3 . For exposures less than 1 hr. in 2N HNO_3 , and for much shorter times in more concentrated nitric acid, a coarse-grained arsenious oxide film results. For long periods of immersion in weak acid the copper oxide film cannot be detected. This does not mean that CuO is absent, but only that it is present in amounts less than 10 per cent in the material that diffracts the electron beam.

Of particular interest are samples of antimonial 70-30 brass, which, after 10 min. in 2N HNO_3 , exhibit thin films whose structure analyses indicate the presence of metallic antimony as the sole component of the corrosion film.

The foregoing results represent experiments made in extremely oxidizing environments. Another set was performed in open beakers with various normalities of hydrochloric acid. From nonarsenical alpha brass after 5-day immersion in 2N HCl a pattern of coarse-grained brass (or copper) was obtained. The films were invisible, yet the grain structure of the material was apparent under the microscope, indicating

that corrosion had taken place. For longer immersions or in more concentrated acid when color changes were noted, fine-grained copper films typical of "dezincified" material were found.

When the thick porous arsenical film was scraped from an alpha brass immersed in a saturated solution of As_2O_3 in 6N HCl, the underlying surface of brass was found to be covered with copper. If the coating is scraped a short time after immersion, this copper film is not discernible. An analogous experiment was performed by the immersion of a straight alpha brass in 6N HCl, to which one gram of Sb_2O_3 was added. Metallic antimony immediately deposited on the brass. When thin coatings were rubbed off, the underlying metal was of the original color. When the reaction was allowed to proceed for sufficient time (6 to 12 hr.) to produce a thick porous coating, the underlying brass was found to be covered with bright copper. Evidently corrosion of the nonarsenical and non-antimonial brasses in this experiment proceeds through the pores of the arsenical and the antimonial film, thereby causing "dezincification" of the brass.

Arsenical coppers containing more than 0.04 per cent As, when immersed in 2N HCl for times of the order of 24 hr., are covered with extremely thin films primarily of As_2O_3 . If, instead of immersion in 100 c.c. of solution, 25 c.c. is used just to cover the samples, the solution becomes cloudy after 6 days. In order to distinguish between precipitation and electrolytic deposition of corrosion products, the structure of the extremely thick film formed was examined. Between the top CuCl film and the copper a porous arsenious oxide (As_2O_3) film was found.

DISCUSSION OF RESULTS AND CONCLUSIONS

In the corrosion of copper it is evident that a crystalline film of copper oxide forms on the surface in certain corrodents. When the copper contains arsenic, redeposition of metallic arsenic takes place which,

in oxidizing media, is rapidly converted to arsenious oxide (As_2O_3). When immersed in hydrochloric acid solutions open to the air, the corrosion process is extremely slow and the arsenical film found upon the surface is identical with that found in oxidizing media.

Brasses containing less than 0.024 to 0.03 per cent As when immersed in nitric acid are filmed primarily with CuO , which may slow down corrosion but does not prevent it. For higher arsenic contents the brass corrodes as an entity and copper redeposits and is oxidized. Since the corrodent rapidly becomes richer in arsenic, this element begins to redeposit and is oxidized to As_2O_3 . For the antimonial brass studied, the mechanism of deposition is essentially similar, yet redeposited antimony does not oxidize as readily. In every case studied the initial film formed is more tenacious than later films, but in none does the film appear impervious to the corrodent.

For brasses in hydrochloric acid of different normality, the first film formed is probably copper. When such brasses contain more than about 0.02 to 0.03 per cent As, the upper part of the film is essentially arsenious oxide (As_2O_3). For equivalent times in hydrochloric acid the film is extremely thin as compared with that formed in HNO_3 . Although little oxygen is available, arsenic apparently is deposited as such but is oxidized to arsenious oxide. The chemistry of this is in harmony with the reactions of metallic arsenic stated by Prescott and Johnson⁸ for solutions up to 6N HCl.

Reflection X-ray experiments show that metallic arsenic readily deposits on alpha brass from saturated solutions of As_2O_3 in 2N to 6N HCl. Electron diffraction pictures of this deposit show that it is also covered with a film of As_2O_3 , therefore it seems reasonable to conclude that during the corrosion of arsenical brass the initial deposit is also metallic but is oxidized when sufficient oxygen is available. We do not

believe that the oxide film serves subsequently as a cathode; the corrosion process continues—albeit more slowly—since the film has some porosity, otherwise the film would not increase in thickness with time. When the metallic arsenic film deposited on nonarsenical brass immersed in the $\text{HCl-As}_2\text{O}_3$ solution is gently rubbed off with cotton, the basis film is alpha brass. As deposition is continued, the basis film becomes more copperlike in color and structure, indicating that dezincification has taken place not only through the pores of the arsenious oxide but also through the pores of the metallic arsenic film.

A similar mechanism exists for antimonial brass, as indicated by the immersion of ordinary brass in a solution of Sb_2O_3 in 6N HCl. The absence of the observable oxide film in the antimonial brass immersed in hydrochloric acid is probably not contradictory. The porous antimony film formed does not necessarily function electrolytically in the corrosion process.

The information obtained on the structure of corrosion films of arsenical brass, arsenical copper and antimonial brass indicates: (1) that the conclusions of Masing⁴ based on overpotential studies of antimonial brasses need revision, and (2) that Fink's³ viewpoint on the dezincification of arsenical brass requires extension.

ACKNOWLEDGMENT

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(L. L. Wyman presiding)

H. R. HANLEY,* Rolla, Mo.—My interest in this paper is not particularly that of corrosion, but I am interested in the film of arsenic. It is totally unrelated and perhaps my remarks are not apropos here. But I do notice that when steel is pickled in hydrochloric solution, there is no hydrogen embrittlement, but when the steel is pickled in sulphuric acid there is such embrittlement. I have been told that perhaps an arsenic film prevents the absorption of hydrogen atoms.

N. W. MITCHELL,† Waterbury, Conn.—I wonder whether the authors have obtained any data as yet to indicate just what effect the concentration ratio of copper to arsenic in the solution has on the rate, and also on the type of product deposited.

F. R. MORRAL,‡ Kokomo, Ind.—The authors mentioned that under certain conditions the electron diffraction pattern reveals copper oxide coating below the arsenious oxide film. For long periods of immersion in weak acid the copper oxide film cannot be detected.

My experience with corrosion products on zinc coatings indicated that although by electron diffraction we obtained only a pattern of basic zinc carbonate, by X-rays we obtained the patterns of the layers underneath; namely, zinc oxide and zinc. Have the authors made both types of analysis of the sample? If they were able to strip the film, have they tried to obtain electron diffraction patterns on the metal side of the film?

C. E. SWARTZ,§ Cleveland, Ohio.—There is one point in which some of us are interested—the use of metals in conditions where solutions do not come in contact with them. I am thinking now of nonaqueous types of corrosion, such as the corrosion obtained at elevated temperatures in various types of atmospheres. Another type of corrosion that is very difficult to deal with is that where oils of various kinds come in contact with metal—oils having dissolved in them or suspended in them certain corroding agents. The latter kind of corrosion is found in most of the internal-combustion engines, where the oil corrodes the bearings.

J. H. HOLLOMON AND J. WULFF (authors' reply).—Mr. Hanley's remarks are of interest to us for we have for some time been interested not only in the effect of arsenic, phosphorus, and antimony on pickling but also on other corrosion phenomena. Our corrosion experiments indicate that, even if iron or steel contained arsenic to a more limited extent than that found in ordinary arsenical brass, arsenic would redeposit upon the surface of the metal during corrosion. Such redeposition would occur whether the alloy corroded by hydrogen evolution or by reduction of oxygen to hydroxyl ion. The hydrogen overvoltage of arsenic is considerably less than that of iron and it seems that the presence of an arsenical film would facilitate hydrogen removal at the surface. To our knowledge, there are no published data upon the rate of corrosion by hydrogen evolution as a function of the arsenic content in either iron or steel. It is possible that the corrosion rate of iron may be decreased by the addition of arsenic even though it allows the evolution of hydrogen at the surface. We have been investigating this point and hope to publish data upon it in the near future.

In answer to Mr. Mitchell, we can only say that in a future paper we will include a discussion of the mechanism of the corrosion of arsenical brass. For the present, it can be said that a certain critical arsenic content is required in order to permit its redeposition. This critical composition depends primarily on the corrosive medium. After such deposition occurs, the nature of the film determines the concentration of cuprous ions necessary to allow the deposition of metallic copper.

In answer to Mr. Morral: Supplementary X-ray diffraction experiments indicate that the underlying film consists of metallic arsenic. Further experiments are necessary, however, to ascertain definitely the structure of all the components of the underlying film.

Mr. Swartz' comment suggests an interesting possibility for some experimental work. The preliminary experiments carried out indicate that the arsenical alloys, when heated in air under 500°C., are filmed primarily with arsenious oxide. It is necessary to determine at what temperature this compound ceases to be the essential constituent and the oxides of copper become paramount, for arsenious oxide might have a tendency to sublime at elevated temperatures.

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Some Practical Observations on Inverse Segregation

BY DANIEL R. HULL,* MEMBER A.I.M.E.

(New York Meeting, February 1941)

IN 1926 Genders¹ reviewed the existing theories of this subject and stated his views in support of the gas-pressure theory. Again, in 1937, the subject was thoroughly reviewed by N. B. Vaughan,³ and by Phillips and Brick,² so that no résumé is called for here. The purpose of this paper is to describe certain observations made in the course of mill work, and to point out that they mostly tend to confirm the gas theory of Genders.

VAPOR SEGREGATION

There is, however, one type of inverse segregation that can be accounted for by considering the volatility of one of the constituents of an alloy. The most familiar case is ordinary brass, which is subject to a zinc enrichment of a few tenths of a per cent at the surface of a chill casting. This has been noted in 70-30 brass by Genders, and a typical example of it is given in Table I, which represents a

TABLE I.—*Example of Inverse Segregation*

| Sample | Copper, Per Cent | Lead, Per Cent |
|------------------------------------|---------------------|-------------------|
| Surface $\frac{1}{32}$ in. | 61.43 | 3.18 |
| 2nd layer | 61.50 | 3.19 |
| 3rd layer | 61.42 | 3.32 |
| 4th layer | 61.65 | 3.25 |
| 5th layer | 61.83 | 3.18 |
| 6th layer | 61.89 | 3.11 |
| Center | 61.86 | 3.14 |

cylindrical billet 7 in. in diameter by 55 in. long. After lathe-turning $\frac{1}{32}$ in.

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* Metallurgist, The American Brass Co., Waterbury, Conn.

¹ References are at the end of the paper.

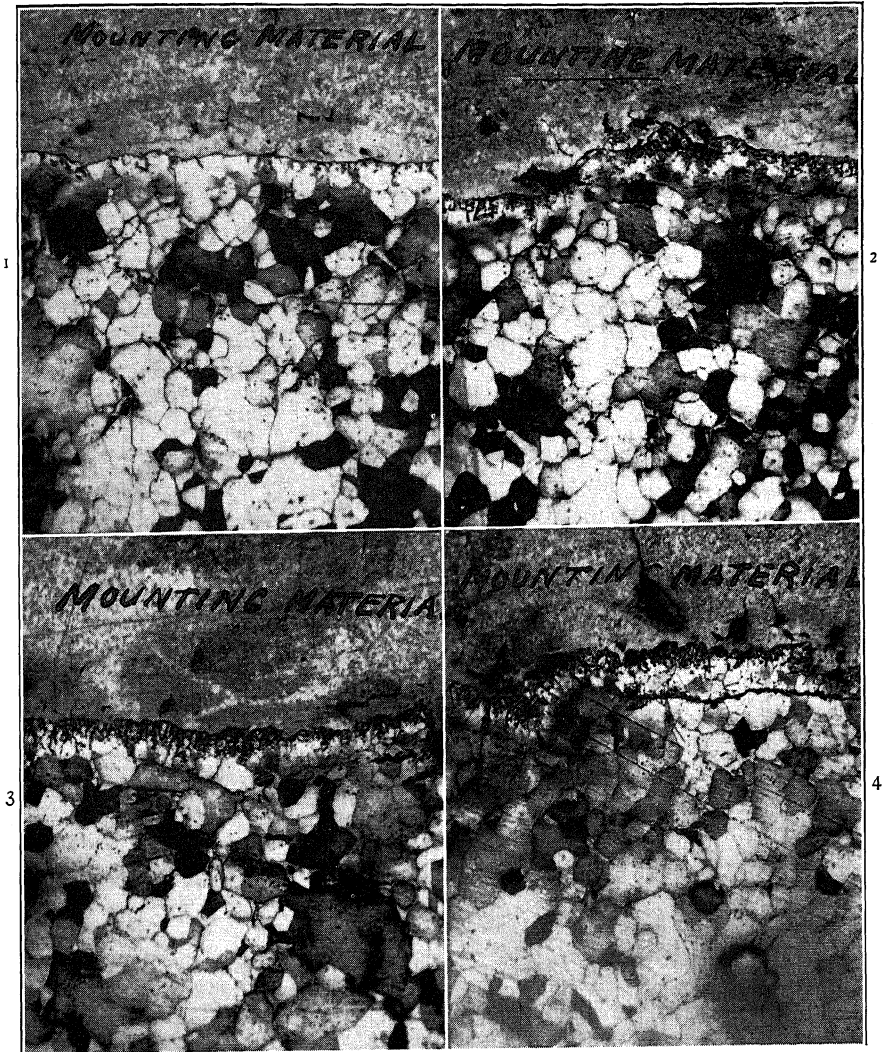
from the surface, the remaining distance to the center was sampled at six equally spaced intervals. The lead, which is essentially the same throughout, will be mentioned later.

Consider a brass-mill mold, either round or rectangular in cross section, standing several feet high. It may require a minute or two for pouring. Before it is full, the metal in the lower end has partly solidified and contracted somewhat away from the mold. The initial shell of solidification follows not far behind the top of the column, even if the central portion is liquid for a long way down. There is, then, a space between metal and mold that is filled with zinc vapor. The vapor has no exit, because the liquid at the top of the rising column is not only in contact with the mold but keeps up a fresh supply of zinc vapor, which has, perhaps, already begun to condense in the lower portion. The cycle is short. Within a minute or two after the mold is full the bar has cooled enough to condense all the zinc. Some of it may condense on the mold; it might be expected that most of it would condense there, but the mold at that time is well coated with a velvety carbon residue from the oil dressing, overlain by fluffy zinc oxide that commenced covering the inside of the mold as soon as pouring began. The clean skin of the freshly cast brass offers a preferred surface for condensation. Reabsorption is quick and inevitable.

A simple experiment indicates that a surprisingly large quantity of zinc vapor is trapped in the space between mold and

metal. This was suggested by the observation that beads of zinc were frequently found adhering to the lower end of billets such as are described in Table 1. A clue

setting it upright, to throw in some "black lead," which was supposed to float up with the metal, give a smooth casting and facilitate its withdrawal.



FIGS. 1-4.—TUBE CASTINGS. CROSS SECTIONS AT SURFACE. $\times 75$.
Nominal composition: copper, 67 per cent; zinc, 32.50; lead, 0.50.

Fig. 1. Normal surface.

Fig. 2. Surface exudations of lead.

Fig. 3. Surface exudations of lead.

Fig. 4. Surface exudations of lead.

to the origin of beads lay in their occurrence only on the bottom end of the billet. It was customary, after oiling a mold and

Perhaps it did so—but enough of it remained near the bottom to smother and envelop the zinc vapor there, and

cause it to condense in discreet drops that could not be reabsorbed, although they might be and often were attached to the parent metal through an alloy bond. The effect could be facilitated by continually throwing black lead into the mold throughout the pour, which produced zinc condensation clear to the top, and in enormously greater quantity. Instead of occasional beads, when such a billet was pulled out of the mold, large areas were sheathed with zinc.

White beads chipped from a billet like that described in Table 1 were, some years ago, reported by the laboratory as a zinc-rich copper alloy containing no lead. Other beads, attached by an alloy bond to a billet containing 0.50 per cent Pb, were found to consist of 3.70 per cent Cu; balance zinc, again without any lead.

The absence of lead is significant, and fits in with the idea of a condensation product rather than an exudation. The manipulation with black lead is cited to indicate that there is enough zinc trapped between metal and mold to accomplish the surface enrichment observed.

GAS SEGREGATION

The absence of lead enrichment in brass surfaces that show normal zinc enrichment is a common condition, but not invariable. Price and Phillips⁴ found lead enrichment in surface protuberances, which seems to the author to be characteristic of brasses that are liable to gassing. While it is true, as mentioned by Genders,¹ that yellow brasses seldom give evidence of gas, they are not immune. The richer copper-zinc alloys may be made to spew by simple overheating and pouring into oiled molds: 70-30 may shrink indifferently and show hydrogen porosity if treated with wet charcoal. Even 65-35 will fail to shrink, and show hydrogen porosity if made, for instance, in a freshly lined Ajax Wyatt furnace that has not been sufficiently dried. The presence of

tin or lead will increase the liability of brasses to dissolved gas. Admiralty shows more evidence of it than straight 70-30, and leaded alloys of 80 per cent Cu or more will spew in the mold with moderate overheating under charcoal. Exudations from all such alloys are rich in tin or lead.

This is shown in a flat slab of leaded rich low brass, 8¾ by 1 in. in cross section by some 50 in. long, which was covered with little spikes protruding from the surface. The composition of surface and center is given in Table 2.

TABLE 2.—*Slab of Leaded Rich Low Brass*

| Sample | Copper, Per Cent | Zinc, Per Cent, (Diff.) | Lead, Per Cent |
|-------------------------------|------------------------|----------------------------------|----------------------|
| 0.03 in. planed from surface. | 83.01 | 13.86 | 3.13 |
| 0.10 in. next layer..... | 84.43 | 13.63 | 1.94 |
| 0.10 in. next layer..... | 84.93 | 13.12 | 1.95 |
| 0.10 in. next layer..... | 85.10 | 13.25 | 1.55 |
| Center | 85.55 | 12.73 | 1.72 |

The spikes on the surface are evidence of gas evolution, and the zinc enrichment at the surface is greater than is ever found in normal brass.

Again, brass tube castings (67 per cent Cu, 0.50 per cent Pb, balance zinc) are particularly liable to exudation of lead in minute protuberances. Some of these are shown in Figs. 1 to 4. Fig. 1 is a normal surface; Figs. 2, 3 and 4 are from the same tube, showing the surface in cross section, through a protuberance. The outside layer of exuded metal is nearly all lead. If the alloy is poured into a mold without any oil dressing, this type of protuberance is absent, and no lead enrichment can be found in the surface. The condition is modified by reducing the quantity of oil. It is not at all stretching the point to say that mold oil may contribute to the gassing of metal, or accentuate the effect of any gas that it may contain. The conditions under which this phenomenon occurs and fails to occur are cited as evidence that gas is the cause.

The effect of gas in a leaded alloy was illustrated impressively, if rather roughly, some years ago, when an occasion arose for preparing an alloy of 70 per cent Cu, 29 per cent Pb, 1 per cent Ni. It was melted in a Northrup high-frequency furnace and end-poured into bars $4\frac{1}{4}$ by $4\frac{1}{4}$ by 60 in. The composition, when liquid, had an avid capacity for reducing gas, much of which was expelled in freezing. When melted under charcoal and poured into an oiled mold, the surface of every bar was sheathed in lead; but if the copper and nickel were first melted and well oxidized, the lead then added and the whole deoxidized with phosphorus and poured into a mold coated only with dry carbon, there was never any lead on the surface. It was evenly, if coarsely, distributed through the bar. There is no doubt that gas was the only considerable factor in this instance. It is cited to show how gas may work when a liquid remnant remains in an already solidified shell. If gas is not the sole cause of lead segregation at the surface, the author has not observed any evidence to the contrary.

TIN SWEAT

The tin bronzes are so inclined to inverse segregation that a great deal of investigation and discussion centers about them. The simplest case of inversion is the "spewed" ingot that does not even shrink in the mold. This is so generally admitted to be caused by a saturation of reducing gas that it is here taken for granted. It is worth noting, though, that a tin-rich liquid of low melting point is visibly forced out from the interior of the ingot. There must be a concentration of it there, which is "normal" segregation. At the start, then, the question is not whether "normal" segregation occurs, but what causes its inversion. The spewed ingot covers rather a large range of gas content, from the one that rises like a biscuit to the one that shrinks almost to com-

pletion, only to spew a few beads at the bottom of the shrink hole. The difference is of degree only. In any case, the casting is honeycombed with gas cavities and useless for commercial work.

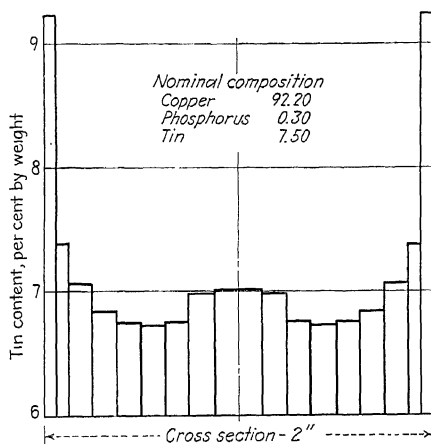


FIG. 5.—AVERAGE TIN CONTENT OF CONCENTRIC LAYERS TURNED FROM A BILLET OF $2\frac{1}{2}$ -INCH DIAMETER. CAST IN AN OILED MOLD.

Nominal composition: copper, 92.20 per cent; tin, 7.50; phosphorus, 0.30.

The next simplest manifestation of inversion is ordinary tin sweat on the surface of a chill casting. This also is widely admitted to be caused by internal gas pressure, even by those who distinguish between it and a more moderate, less obvious tin enrichment in the surface. The evidence favorable to such a view is impressive. Suppose a casting is taken from a chill mold after it is apparently solid. It may have cooled until red is barely visible, when the sweat suddenly appears in such a ghostlike manner that one can only say: "A moment ago it was not there, and now it is there." Apparently the bar that seemed to be entirely solid was really far from it. But, again, the liquid metal was certainly in the interior, where it should be in "normal" freezing; and to be liquid at the temperature at which it appeared on the surface it would have to contain upward of 20 per

cent tin. By whatever process the tin-rich tag end reached the surface, it must have penetrated and passed through the already "solid" walls. It does not too seriously

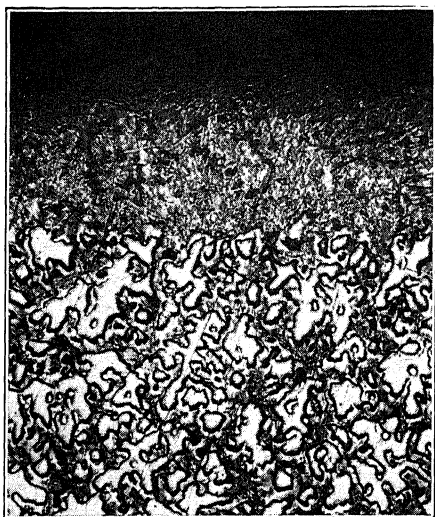


FIG. 6.—CROSS SECTION AT SURFACE, CAST BILLET OF 2-INCH DIAMETER, SHOWING LAYER OF 20 PER CENT TIN. $\times 75$.

Nominal composition: copper, 92.20 per cent; tin, 7.50; phosphorus, 0.30.

strain one's credulity to imagine that, when freezing approached completion, gas thrown out of solution (either through concentration or reaction) developed pressure enough to expel this liquid residue through the side walls, appropriating the space to itself. The characteristic unsoundness at the center of such castings has generally been assigned to the wide freezing range that results in interdendritic shrink cavities, cut off from access to any source of "feed," but the freezing range might well involve a secondary implication—that of holding gas in solution until all avenues of escape have been closed. It is thrown out of solution only to be trapped in the center of the casting, under substantial pressure.

There is the view of Price and Phillips,⁴ that the liquid interior is pressed to the surface by the contracting shell. This would increase the pressure on the entrapped gas,

and the solid shell of the casting (commercial rolling-mill slabs) would appear strong enough to sustain it. But Genders further points out that the shell contraction ought to close the interior voids. This seems reasonable and, since bronze with heavy tin sweat is particularly unsound at the center, the function of the gas seems probable.

TABLE 3.—Composition of Layers from Tin Billet

| Layer | Thickness, In. | Tin, Per Cent |
|-----------------|----------------|---------------|
| 1, surface..... | $\frac{1}{16}$ | 9.23 |
| 2, next..... | $\frac{1}{16}$ | 7.55 |
| 3, next..... | $\frac{1}{8}$ | 6.92 |
| 4, next..... | $\frac{1}{8}$ | 6.98 |
| 5, next..... | $\frac{1}{8}$ | 6.89 |
| 6, next..... | $\frac{1}{8}$ | 6.95 |
| 7, next..... | $\frac{1}{8}$ | 6.88 |
| 8, next..... | $\frac{1}{8}$ | 6.93 |
| 9, center..... | | 6.98 |

It has often been pointed out that the degree of inverse segregation depends on the degree of gassing. This is true in commercial work. In a bronze of 8 per cent tin, for instance, the surface may readily contain upward of 20 per cent tin. Table 3 gives the composition of layers turned from a billet of 2-in. diameter by 60-in. length. Fig. 5 shows the condition graphically. This does not tell the whole story. Thin scrapings from the surface were found to contain 20.34 per cent tin.

Fig. 6 is in cross section of this billet, showing the sharp division between the rich surface and the metal immediately under it, which does not greatly vary from there to the center. The rich layer is only about 0.012 in. thick, and is easily missed in sampling. As has been noted, ordinary tin sweat would necessarily contain 20 per cent to be liquid at the temperature observed. While this is typical of bronze melted and poured under reducing conditions, the rich surface layer does not occur after the use of an oxidizing atmos-

phere, which is in favor of the gas theory. This has been noted by several others, and often confirmed. In a comparatively gas-free casting of rolling-mill size, the intensely rich skin layer is absent, and the surface is only moderately high in tin (Figs. 7 and 8).

That inversion can never be prevented entirely by this means is not an argument against the gas theory. Commercially, there is certainly no gas-free tin bronze. It may be possible to destroy the reducing gases by oxidation; but up to the point where tin oxide appears in the melt, such destruction is only relative. If oxidation is carried over into tin oxide the melt becomes viscous, and strongly reactive with any reducing substance available. The few experiments that have been made with such metal have shown evidence of gas, either by spewing or throwing "spikes" from the surface. This is believed to have resulted from reaction with carbon in the mold, but has not been followed up. In any case, such metal would have to be deoxidized to be commercially useful, which would render it again liable to absorption of reducing gas. So, although there is no gas-free bronze in everyday work, it is significant that inverse segregation is only slight when gassing is slight, and is invariably intense when conditions are favorable to gas.

It has been pointed out by Rosenhain⁵ and others that inverse segregation is present in a slush casting and this has been cited as evidence against the gas theory. While it might be construed as evidence against shell contraction, it is not incompatible with the gas theory, because, while the full effect of gas is not exerted until the last metal has frozen, gas is thrown out of solution, and begins to be effective with the first chill in the mold. With the freezing of the first shell, gas pressure is immediately established within that shell, and some of the selective high solute residue resulting from that first solidification is pushed to the outside.

If the pressure available for pushing it out there is slight, the resistance to its course is also slight.

The quick start of inverse segregation,

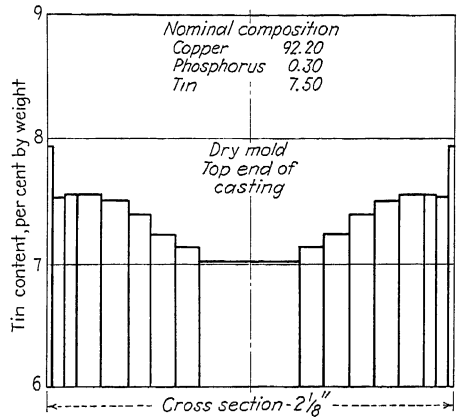


FIG. 7.

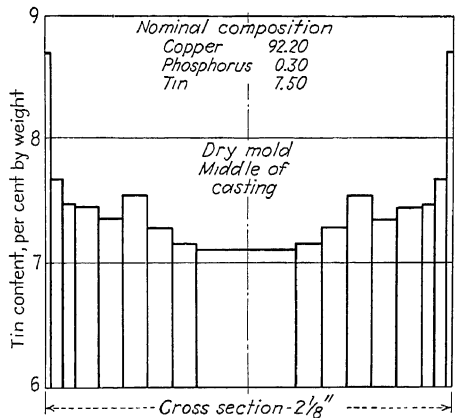


FIG. 8.

FIGS. 7 AND 8.—AVERAGE COMPOSITION OF CONCENTRIC LAYERS TURNED FROM A BILLET OF $2\frac{1}{2}$ -INCH DIAMETER, CAST IN MOLD COATED WITH DRY CARBON.

Nominal composition: copper, 92.2 per cent; phosphorus, 0.3; tin, 7.5.

and its progression through the freezing period can be traced in the shrink end of a vertical casting. This has been done with a $2\frac{1}{8}$ -in. dia. rod, about 60 in. long, cast in an iron chill mold, dressed with oil, the alloy being 8 per cent Sn-Cu, 0.3 per cent P. When the mold was full the rod

was allowed to shrink naturally, without feeding. The shrink hole formed a cone-shaped hollow, about 6 in. deep. Concentric layers were turned off at a point near the top, and again about a foot from the top, where solidification had been completed in a normal manner. The layers were analyzed, with results as shown in Table 4.

TABLE 4.—*Analysis of Concentric Layers*
ROD $2\frac{1}{8}$ -IN. DIAMETER; COMPOSITION, 8 PER CENT TIN, 0.3 PER CENT PHOSPHORUS, REMAINDER, COPPER

| Layer | 10 In. below Top, Per Cent | | 2 In. from Top, Per Cent | |
|---------------------------|----------------------------|------|--------------------------|------|
| | Sn | P | Sn | P |
| Skin layer 0.010 in. | 9.09 | 0.40 | 8.14 | 0.34 |
| Next 0.10 in. | 7.79 | | 7.72 | |
| Next 0.10 in. | 7.28 | | 7.13 | |
| Next 0.20 in. | 7.13 | | 7.24 | |
| Next 0.20 in. | 6.95 | | Hollow | |
| Next 0.20 in. | 6.94 | | | |
| Next 0.20 in. | 7.12 | | | |
| Center..... | 6.95 | 0.29 | | |

This indicates that inverse segregation had begun, and had proceeded to a substantial degree in the short time during which the mold was full, before the shrink went down below the point where the top samples were taken, but considerably more surface enrichment took place a little further down, where it could go to completion. In an experiment like the above, little spikes or beads can sometimes be found protruding from the surface, within a fraction of an inch from the top. By watching closely, one may see them thrown out. They appear after the shell has formed, just as the shrink hole is starting to sink. The interval is only a few seconds, but the suddenness and energy with which they appear are strongly suggestive of gas.

If it is admitted that an intense surface concentration of tin can be caused by gas pressure, it seems probable that a more moderate segregation might be due to the same cause.

CONCLUSIONS

1. In brass chill castings, the slight surface enrichment in zinc is attributed to condensation and reabsorption of zinc vapor.
2. In leaded brass, the occurrence of lead at the surface is attributed to gas pressure.
3. In tin bronze, inverse segregation of tin is attributed to gas pressure.

ACKNOWLEDGMENTS

Acknowledgments are due to Messrs. H. L. Silliman and J. C. Rowell, of The American Brass Company's technical staff, for collection and preparation of data, and to Dr. Cyril Stanley Smith for constructive support and criticism.

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DISCUSSION

(J. T. Norton presiding)

W. B. PRICE,* Waterbury, Conn.—I congratulate the author on a fine, practical paper. I cannot entirely agree with his conclusions that inverse segregation is caused entirely by gas pressure. Under certain circumstances, it may be caused by contraction of the shell or by a combination of shell contraction and gas pressure.

G. EDMUNDS,† Palmerton, Pa.—Has anyone made vacuum casts of these alloys that are susceptible to inverse segregation—not only in a vacuum but of thoroughly degasified alloys?

J. T. KEMP,‡ Waterbury, Conn.—I join Mr. Price in welcoming Mr. Hull's paper as one of the practical type—and that appeals to

* Chief Chemist and Metallurgist, Scovill Manufacturing Co.

† Research Division, New Jersey Zinc Co.

‡ Metallurgical Engineer, American Brass Co.

men who have arrived through the refinery and the mill. We have seen phenomena that have been described as inverse segregation in the present paper; we have seen them occur many times and in many places, and when they are brought before us as simply and as beautifully as has been done by Mr. Hull we think back to the many cases in which we have seen evidence of internal precipitation of gas as the cause of the appearance of molten metal on the outside of partly solidified castings.

This phenomenon is not confined to alloys whose melting temperatures are largely affected by the alloy addition and that have a wide liquidus-solidus temperature spread. We have seen the same thing in almost pure metals, metals whose structure is not unlike that of the casting shown in Fig. 6.

At one time, I had the task of knocking off the sink-heads from malleable nickel and Monel ingots before they were entirely frozen, and occasionally, if I knocked them off a little too quickly, before they were completely frozen, I would bleed some of the molten metal from the head and then find that the space within the head was filled with a network of dendritic crystals, crystals that might be $1\frac{1}{2}$ to 2 in. long. Such an observation shows that as the time of final solidification approaches there is a mesh of solid crystals in a bath of liquid metal. It shows readily the conditions that must exist at the moment of gaseous precipitation and the development of a pressure thereby on the liquid within the casting. It also indicates the probability of the simultaneous existence of interdendritic channels in the outer shell of the castings through which the inner liquid can flow. Such channels may still be filled with liquid at the critical moment or with metal still soft enough to yield to hot liquid penetration.

There are many examples of this behavior. The common development of snakes on blister copper, an impure copper to be sure, of 96 per cent or so, is one. There may be a eutectic in blister from which the liquid is ejected; perhaps there is, but the general appearance of a freezing cake suggests rather that the snakes come from the liquid reservoir within. There is a time relation too between the appearance of ejected liquid copper and the formation of the dark area on the crust that marks the "blister." Then there are the little spurts of

flame, burning gas that escapes through the crust to the atmosphere, to say nothing of the lift of the crust itself.

I have seen spewing on nickel ingots running 99.6 per cent Ni. I have seen it on nickel shot analyzing 99.8 plus, poured in water. Some grades of nickel must be "quieted" in the furnace before pouring or the shot will not sink in the water tank. Under some conditions there is such a volume of gas released from the shot as the drops of metal solidify under water that it burns at the water surface as the columns of bubbles emerge.

I have seen flames on top of many a solidifying nickel ingot. Such ingots often can be broken open with a sledge. When they are broken open, particularly those that have cast badly and have swelled and run over the mold, they exhibit ample interdendritic porosity. Metal properly conditioned in the furnace lies quietly in the mold, solidifies without visible discharge and is sound and hard to break when cold. Those that snake badly will be as full of holes as a sponge.

Mr. Hull is right in his belief that it is the development of pressure by internal gas precipitation from the final liquid phase of a casting that is the cause of the appearance of liquid on the solid surfaces of cast bars. The evidence that he presents, the rich alloy of the exudate, is convincing.

R. M. BRICK,* New Haven, Conn.—I have always felt that inverse segregation was at least one problem we could teach students with some assurance, on the basis that the dendrites forming in the liquid are enriched in the higher-melting-point element. The liquid adjacent to those dendrites is enriched in the lower-melting element (or elements), and as solidification proceeds interdendritic contraction occurs; that is, two dendrites contract away from one another and open a channel between them, a low-pressure area, into which the enriched liquid flows to the surface. That ties up very nicely with the physical conditions and our phase diagrams.

There is no doubt that the process is expedited or accentuated by internal gas pressure, or in some cases by contraction of the shell; but I do not believe that it can be urged successfully that gas pressure is predominant in all

* Hammond Laboratory, Yale University.

cases or is the ultimate cause, since we have found inverse segregation in single crystals of solid solution alloys where solidification has taken place in one direction only, the temperature gradient extended in one direction only, the single crystal froze from the bottom up and the surface was always kept liquid. Yet, the bottom of the single crystal was enriched in the lower-melting-point element. This seems to be pretty strong evidence against accepting the gas-pressure theory or contraction pressure as the predominant or the fundamental cause.

C. S. SMITH,* Waterbury, Conn.—The role of zinc vapor in producing local differences of composition is a new and most interesting observation. I suspect that under some conditions an effect greater than the diffusion of zinc in and out of the solid casting is the condensation on the mold walls of zinc vapor evolved by the stream of liquid brass, the zinc being subsequently re-absorbed in the quickly chilled outer layers of liquid as the mold fills. Diffusion from or into the solid alloy could, of necessity, affect only a very thin layer. A case where this undoubtedly is involved is gamma brass. Castings of this alloy invariably have a uniform thin layer (0.005 in.) of a ductile material on the surface, presumably beta. I believe this results from zinc vaporization at the surface of the solid material, the vapor condensing on the mold rather than on other parts of the casting. It occurs to a greater extent in a dry dressed mold than in oiled molds, and is absent on the parts of the casting that are exposed to air and covered with an impermeable oxide coat.

A combination of many theories is necessary to account for the observed facts of segregation. The gas-pressure theory has generally found favor among men who have observed large-scale commercial operations, while laboratory workers tend to favor more involved theories. The difference, I think, is largely a result of

lack of agreement as to what is meant by inverse segregation. Surface exudations like those shown in Figs. 2 to 4 represent only one type. Anyone who sees metal squirt out of the surface of a large billet cooling on the casting-shop floor will quickly be convinced that gas pressure is in large measure responsible for these exudations and for the related effects of shallow surface enrichment resulting from the spreading of exuded low-melting-point material. This exudation type of segregation is quite different in cause and nature from the more gradual change of composition from center to outside that is found in substantially gas-free melts, and requires a more elaborate explanation.

D. R. HULL (author's reply).—In preparing my remarks, I was tremendously impressed with one thought all through it—what a paper a man could write if he knew all about this subject.

For a long time I subscribed to the shell-contraction theory, but there are some things about it that are difficult to explain. For instance, if the liquid is forced to the surface by shell contraction, why, as has been pointed out before by others, is the inside so unsound? The central portion of an ingot that has shown a great deal of inverse segregation is notoriously unsound.

Mr. Edmunds asked if we had any results from vacuum melting. We have not. I still have a feeling that when somebody makes a really effective vacuum melt of tin bronze, the center will be tin-rich, as it ought to be.

The interdendritic theory that Dr. Brick has spoken of, I can accept up to a certain point. I can readily see how the interdendritic view might account for tin enrichment near the surface, but it is difficult to visualize how that could push the tin-rich alloy clear out onto the surface in the form of a sweat, or leave the center poorer in tin than the surface.

* Research Metallurgist, American Brass Co.

The Self-diffusion of Silver

BY WILLIAM A. JOHNSON*

(New York Meeting, February 1941)

THE fundamental role of diffusion in many reactions occurring in solid metals has long been recognized, and there have been careful measurements of rates of diffusion in numerous alloy systems; but our understanding of the atomic mechanism by which diffusion occurs is scarcely in an advanced state.¹⁻³ It is doubtful that this mechanism can ever be directly ascertained; rather, all imaginable mechanisms must be examined and the one that is in best accord with such data as can be obtained from suitably chosen experiments should be selected. Because of its relative simplicity, diffusion in a system containing only one kind of atomic species—commonly called self-diffusion—is of considerable theoretical interest. It may be expected that diffusion theory will not be advanced appreciably until a wide variety of diffusion experiments—of which diffusion in a chemical concentration gradient and self-diffusion are two important types—are carefully performed and inter-compared. Aside from the purely theoretical interest in self-diffusion measurements, such studies will be of considerable engineering importance. The rate of any process in a pure metal requiring the movement of atoms, of which recrystallization and creep are two familiar examples, will be understood more readily with the aid of self-diffusion data.†

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† References are at the end of paper.

† The determination of the rate of self-diffusion of silver is one phase of an investigation of diffusion in the silver-gold system by the usual chemical methods in a chemical concentration gradient, and by radioactivity methods in homogeneous alloys.

Self-diffusion implies the diffusion of something into its exact counterpart; the detection of such a process is patently impossible, and it is necessary to substitute for it the diffusion of one isotope (in this case radioactive) into another isotope (in this case stable) of the same chemical element. There is, however, no reason to suppose that a radioactive atom will not diffuse at the same rate as its stable isotope, for all of the isotopes of the same element have exactly the same chemical properties; neither the difference in nuclear energy nor the difference in mass would be expected to exercise an important influence in this phenomenon. In this sense, self-diffusion may be thought of as the diffusion of radioactive atoms down a radioactivity concentration gradient, just as usual diffusion is the diffusion of one kind of atom down its chemical concentration gradient.

The first measurements of self-diffusion were made by von Hevesy⁴⁻⁶ using the radioactive lead isotope thorium B in ordinary lead. The recent development of means for producing artificial radioactive elements has made possible similar measurements on gold,^{7,8} copper,^{2,9} and zinc.^{10,11} Many of the data that have been obtained are rather poor, and no adequate reason has been given for their poorness; it appears, however, that the unsatisfactory results are characteristic of the particular experimental procedure employed, and not of self-diffusion measurements in themselves. The experimental technique that has yielded the poorer results is the deposition of a thin layer of radioactive atoms on the surface of a specimen and the determination of the rate of inward diffusion

by the decrease of surface radioactivity; this procedure has been used in the study of lead,^{4,5,6} copper,² and gold.⁸ A more satisfactory, if more tedious, method is to

silver chloride. Using this solution with standard plating technique, a layer of radioactive silver about 0.0004 cm. thick was plated on one face of a silver disk

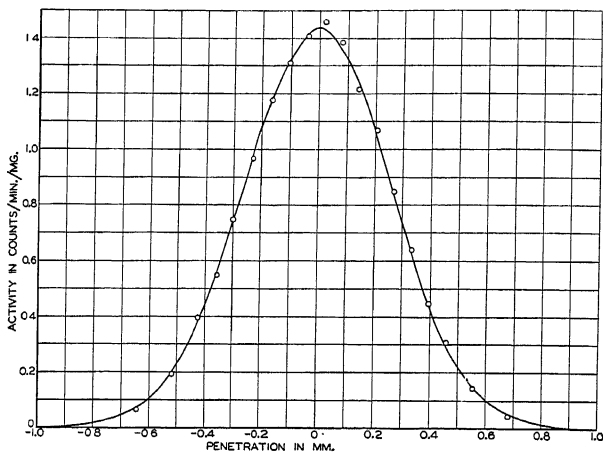


FIG. 1.—CONCENTRATION-PENETRATION CURVE FOR DIFFUSION OF RADIOACTIVE SILVER IN ORDINARY SILVER AFTER 4.78 DAYS AT 876.0°C.

section the specimen after diffusion and determine a concentration-penetration curve, a procedure quite analogous to that usually employed in alloy diffusion; measurements by this principle have been made on copper,⁹ gold,⁷ and zinc,^{10,11} and, as will be described in the present paper, on silver.

EXPERIMENTAL PROCEDURE

Radioactive silver, initially approximately equal parts of Ag^{105} (half-life 45 days) and Ag^{106} (half-life 8.2 days) was prepared by proton bombardment of palladium in a cyclotron.¹² The radioactive silver was chemically separated from the palladium as silver chloride, with 50 milligrams of ordinary silver added as a carrier; the concentration of radioactive silver in the precipitate was very low, of the order of magnitude 10^{-12} , but this concentration does not enter into the subsequent calculations. A standard silver cyanide electroplating solution was prepared from the

$\frac{7}{8}$ in. in diameter and $\frac{1}{4}$ in. thick. The silver disk, in which the grain size was about one grain per square millimeter, was prepared from Baker chemically pure silver; analysis showed the silver to be of high purity, except for 0.04 per cent Cu. A second similar silver disk was welded to the active surface by heating the disks under pressure for 30 min. at 750°C. in a vacuum furnace. This yielded a composite specimen consisting of a thin plane layer of radioactive silver bounded on both sides by effectively semi-infinite layers of ordinary silver. Diffusion was thus one-dimensional, but occurred in two directions. The specimen was then sealed off in a highly evacuated quartz tube and placed in a potentiometrically controlled electric furnace for the diffusion anneal. After the diffusion anneal, layers of thickness from 0.002 to 0.005 in., parallel to the original active layer, were machined off in a lathe. These layers were dissolved in nitric acid and the radioactivity of each layer was measured by a liquid glass countertube

connected to a scale-of-four Geiger-Müller of the diffusion equation counting circuit.

As may be inferred from the technique employed, no large experimental errors

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

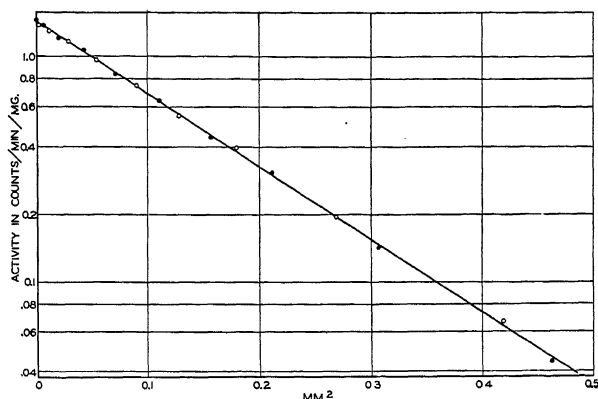


FIG. 2.—RELOT OF DATA FROM FIG. 1.

Log radioactivity as ordinate and distance from interface squared as abscissa; open circles from left side of Fig. 1, closed circles from right side.

are to be expected. The temperature measurements are believed to be correct within 1°C.; an error of 1°C. in the temperature produces an error of about 2 per cent in the calculated diffusion coefficient. Errors in the measurement of distance should produce an error not greater than 2 per cent. The statistical error in the measurement of radioactivity ranged from 1 to 2 per cent, and should introduce a much smaller error in the calculated diffusion coefficient. The amount of diffusion that occurred during the welding operation is negligible; the penetration is determined by the product of time and diffusion coefficient, and this product for the welding operation was much less than 1 per cent of the value for the diffusion anneal. The several experimental errors are independent of one another, and it is probable that the calculated diffusion coefficients are accurate to 3 or 4 per cent.

EXPERIMENTAL RESULTS

If the initial layer of radioactive silver be considered infinitely thin, the solution

appropriate to the boundary conditions employed experimentally is¹³

$$c = \frac{c_0}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \quad [1]$$

where c is the concentration of radioactive atoms,

x is the distance from the original interface,

D is the diffusion coefficient,

t is the time,

c_0 a constant, is the product of the initial concentration of radioactive silver times the thickness of the layer.

The error introduced in neglecting the finite thickness of the layer of radioactive silver is less than 1 per cent, because of the large penetration obtained.

Fig. 1, which is characteristic of all the experimental results, is a concentration-penetration curve obtained from a specimen heated at 876.0°C. for 4.78 days. The open circles are experimental points and the smooth curve is calculated from equation 1,

using the value of D that yields the best fit between the calculated curve and the data. The good agreement between the data and the calculated curve indicates the applica-

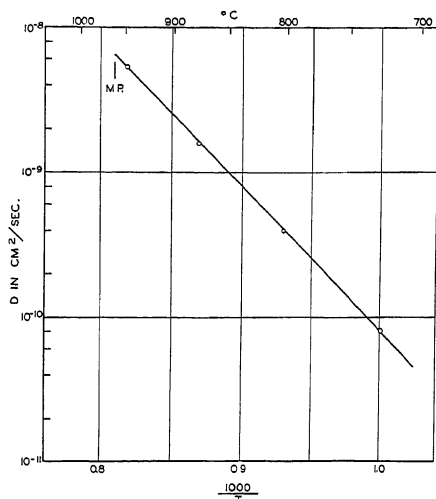


FIG. 3.—VARIATION OF SELF-DIFFUSION COEFFICIENT OF SILVER WITH TEMPERATURE, LOGARITHM OF D VERSUS RECIPROCAL OF ABSOLUTE TEMPERATURE.

bility of simple diffusion theory, and the fact that the two sides of the curve are symmetrical about the original interface shows that the electroplated and welded interfaces are equally good. There is no evidence supporting the belief that a fraction of the radioactive atoms remain "stuck" at the original interface, as has been reported for the self-diffusion of zinc.^{10,11}

The type of curve shown in Fig. 1 is not convenient for calculating the diffusion coefficient. By taking logarithms of equation 1, the following relation is obtained:

$$\log c = -0.4343 \frac{x^2}{4Dt} + \log \frac{c_0}{2\sqrt{\pi Dt}}$$

which may, for the present purpose, be more conveniently written

$$\log c = -0.1086 \frac{x^2}{Dt} + \log k \quad [2]$$

If the logarithm of the radioactivity is plotted as a function of the square of the distance from the interface, the data will be expected to lie along a straight line, and this expectation is accurately fulfilled, Fig. 2. The slope of this line, according to equation 2, is

$$\text{slope} = \frac{-0.1086}{Dt}$$

and since t is known, D is calculated readily. The units of D are square centimeters per second. The diffusion coefficient calculated in this manner is slightly too small, since diffusion distances are shorter at room temperature, where measurements were made, than at the diffusion temperature. The proper correction is readily calculated from the coefficient of thermal expansion of silver and varies from 2.6 per cent at 725°C. to 3.5 per cent at 950°C.

The variation of the diffusion coefficient with temperature is shown in Fig. 3, in which the logarithm of D is plotted against the reciprocal of the absolute temperature. The four experimentally determined points fall nicely along a straight line, whose equation is

$$D = 0.895e^{\frac{-45,950}{RT}}$$

DISCUSSION OF RESULTS

It is of interest to note that the activation energy for the self-diffusion of silver, 45,900 cal. per mol, agrees well with the figure of 45,200 cal per mol given by the Dushman-Langmuir equation.

It is not unreasonable to suppose that this activation energy, Q , should bear some relation to the energy required to destroy the metal lattice, of which the temperature of the melting point, T_m , and the binding energy,* E , are convenient measures.² The available information on the self-diffusion of metals, taken from Steigman, Shockley and Nix,² with the addition of

* The binding energy E is the heat of sublimation at absolute zero.

the present data for silver and recent data for zinc,^{10,11} are given in Table 1. Q is in nearly constant relationship to T_m and E in the cubic metals copper, gold, lead and silver; the same relationship is borne out in the noncubic metals bismuth and zinc if the lower of the activation energies corresponding to the two principal crystallographic directions is chosen. As Steigman, Shockley and Nix point out, it is not possible to say to which of these measures of lattice energy Q is more closely related.

TABLE 1.—Data on Self-diffusion

| Metal | Q , K Cal. per Mol | T_m , Deg. K., Melt- ing Point | E K Cal. per Mol | $\frac{Q}{T_m}$ | $\frac{Q}{E}$ | Refer- ence |
|-------------------------------|-------------------------------|---|-----------------------------|-----------------|---------------|----------------|
| Cu | 57.2 | 1356 | 81.2 | 42 | 0.70 | 2 |
| Cu | 61.4 | 1356 | 81.2 | 45 | 0.76 | 9 |
| Au | 51.0 | 1336 | 92.0 | 38 | 0.55 | 8 |
| Au | 62.9 | 1336 | 92.0 | 47 | 0.68 | 7 |
| Pb | 28.05 | 600 | 47.5 | 47 | 0.59 | 14 |
| Ag | 45.9 | 1234 | 68.0 | 37 | 0.68 | |
| Bi \perp C | 31.0 | 544 | 47.8 | 57 | 0.65 | 15 |
| Bi \parallel C | 140 | | 47.8 | 257 | 2.92 | |
| Zn \perp C | 17.6 | 693 | 27.4 | 25 | 0.64 | 11 |
| Zn \parallel C ^a | ~17.6 | 693 | 27.4 | ~25 | ~0.64 | 10 |

^a These values are inferred from data obtained on polycrystalline zinc.

No data except those published herewith have been presented on the rate of self-diffusion of silver. The activation energy determined in this work appears quite reasonable, however, since it bears the usual relation to T_m and E , since it agrees with that calculated from the Dushman-Langmuir equation, and since it is somewhat higher than the activation energy for the diffusion of other elements in silver.¹⁶

ACKNOWLEDGMENT

It is a pleasure to thank Dr. J. E. Hill, who prepared the radioactive silver in the cyclotron of the University of Rochester, and the Westinghouse Research Laboratories for the granting of a fellowship.

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DISCUSSION

(R. M. Brick presiding)

F. E. CARTER,* Newark, N. J.—Fig. 3 shows the variation of self-diffusion with temperature. Without claiming any particular knowledge on this subject, I might have expected a very considerable increase in the rate of self-diffusion as the melting point is approached. I look on this property as somewhat analogous to extrusion. The extrudability of a metal increases exceedingly rapidly as the temperature approaches the melting point, indicating marked increase in mobility just below that point. The author has continued his straight-line curve right up to the melting point and I would like to ask whether he has considered that any marked deviation is possible between the highest temperature of his measurements, 950°C., and the actual melting point of pure silver.

P. H. BRACE,† East Pittsburgh, Pa.—What is the significance of the term "activation energy"?

W. A. JOHNSON (author's reply).—No direct correlation between the phenomena of extrudability and self-diffusion has been discovered, and there is at least no obvious reason for supposing that a correlation should exist. No data for the self-diffusion of silver have been

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† Westinghouse Electric and Manufacturing Co.

obtained at temperatures very slightly below the melting point, but such data are available for lead and bismuth,¹⁷ and these obey a straight-line relationship between $\log D$ and $1/T$, apparently to the melting point.

A great deal might be said in reply to Mr. Brace's question. A very simple explanation of the term "activation energy" might be the following: A given atom must possess the energy ϵ to move from one lattice position to another; this energy is its "activation energy." The probability that an atom will possess the requisite energy for movement varies with

temperature according to the well-known Boltzmann equation

$$p = e^{-\epsilon/kT}$$

so that a measurement of the variation in diffusion rate with temperature will furnish a means for determining ϵ quantitatively. The diffusion coefficient is thought to be proportional to the probability p , the proportionality constant involving, perhaps among other factors, the frequency of vibration of the atoms and the interatomic spacing; it cannot be exactly evaluated until a satisfactory theory of diffusion is devised.

¹⁷ W. Seith: *Diffusion in Metallen*, 48, 68. Berlin, 1939. J. Springer.

On the Equilibrium Solidification of Solid Solutions

By MORRIS COHEN,* MEMBER A.I.M.E., AND WILLIAM P. KIMBALL†

(Cleveland Meeting, October 1940)

ABSTRACT‡

THIS paper deals with the calculation of the composition of the infinitesimal trace of alloy that transfers from the liquid to the solid state at each temperature during the equilibrium solidification of a binary solid solution, and which thereby enables the compositions of the coexisting liquid and solid phases to follow along the liquidus and solidus lines respectively during the cooling. A general expression for the composition (δ) of the liquid-to-solid transfer at each temperature has been derived:

$$\delta = \frac{Z_L x_L (x_L - P) + Z_S x_S (P - x_S)}{Z_L (x_L - P) + Z_S (P - x_S)} \quad [1]$$

where Z_L and Z_S are the slopes of the liquidus and solidus lines at the given temperature, x_L and x_S are the compositions of the stable liquid and solid phases at the same temperature, and P is the composition of the alloy under consideration. The δ equation is valid for the process of equilibrium heating as well as cooling, and may be applied to vapor-to-liquid, vapor-to-solid, liquid-to-liquid, and solid-

to-solid transfers if the corresponding equilibrium diagrams are known.

The δ -versus-temperature curves for two alloys P_1 and P_2 are shown in Fig. 1.

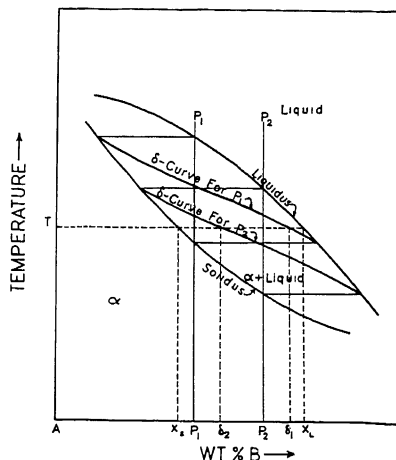


FIG. 1.—GENERAL SOLID SOLUTION DIAGRAM SHOWING δ CURVES FOR ALLOYS P_1 AND P_2 .

In each case, the liquid-to-solid transfer has the same composition as the stable solid phase only at the temperature of the beginning of solidification, and has the same composition as the stable liquid phase only at the temperature of the completion of solidification. At each intermediate temperature, the composition of the liquid-to-solid transfer differs by a finite amount from those of the two coexisting phases. Therefore, during equilibrium cooling, the transfers must merge into the solid phase from the liquid without forming a transition phase; otherwise the condition of equilibrium would be violated. At any given temperature during solidification, the composition of the liquid-to-solid

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‡ Manuscript received at the office of the Institute June 27, 1940. The entire manuscript has been submitted to the American Documentation Institute, 2101 Constitution Avenue, Washington, D. C., for issuance in the form of microfilm or photoprint. The derivation of the equations and their physical significance are discussed in detail in the paper. For entire paper, write to the American Documentation Institute, ordering Document 1440 and remitting thirty-five cents for microfilm (read enlarged on machines widely available) or one dollar and eighty cents (\$1.80) for photoprint (readable without optical aid). This abstract was issued as T.P. 1256 in METALS TECHNOLOGY, December 1940.

transfer is richer in per cent B, the lower the per cent B in the alloy as a whole.

In the general case, the values of Z_L , Z_S , x_L and x_S which appear in the δ

example, if the liquidus and solidus lines are straight over the solidification range and intersect on the temperature axis at the melting point T_A of component A, the δ -versus-temperature curve becomes a parabola:

$$\delta = \frac{(T_A - T)^2}{P m_L m_S} \quad [2]$$

where m_L and m_S are the constant slopes of the liquidus and solidus lines. In such a straight-line system, it turns out that the weight of component B contained in each liquid-to-solid transfer is independent of the temperature and the composition of the alloy, even though equation 2 shows that the percentage of B in the transfer depends upon both these factors. Accordingly, variations in the composition of the liquid-to-solid transfers must be accomplished merely by variations in the weight of component A contained in the transfers.

Calculated δ curves for five iron-carbon alloys are shown in Figs. 2 and 3. The curves in Fig. 3 have interesting discon-

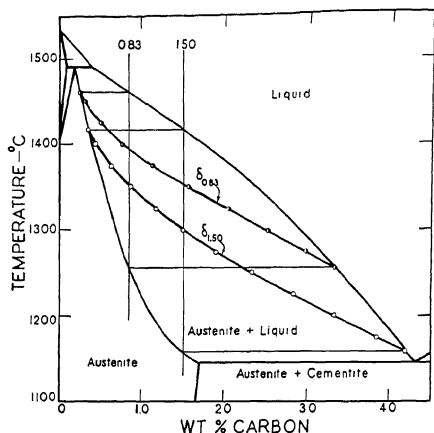


FIG. 2.—PORTION OF IRON-CARBON DIAGRAM SHOWING δ CURVES FOR ALLOYS CONTAINING 0.83 PER CENT AND 1.50 PER CENT CARBON.

equation are determined graphically from the equilibrium diagram. However, if the

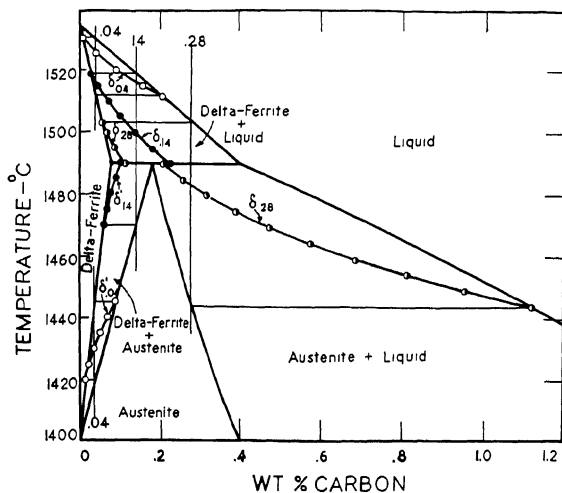


FIG. 3.—PORTION OF IRON-CARBON DIAGRAM SHOWING δ CURVES FOR ALLOYS CONTAINING 0.04 PER CENT, 0.14 PER CENT AND 0.28 PER CENT CARBON

The δ' curves give compositions of solid-to-solid transfers corresponding to conversion of delta ferrite into austenite during equilibrium cooling.

equations of the liquidus and solidus lines are known, δ may be expressed explicitly as a function of the temperature. For

tinuities because of the peritectic reaction that interrupts the normal course of solidification.

Measurement of Irreversible Potentials as a Metallurgical Research Tool

BY R. H. BROWN,* W. L. FINK,* MEMBER A.I.M.E., AND M. S. HUNTER*

(Cleveland Meeting, October 1940)

EARLY workers attempted to study the structure of alloys by measurement of equilibrium electrode potentials in aqueous solutions containing ions of the metals from which the alloy was made.¹ The method was subject to such limitations (e.g., the difficulty in attaining electrochemical equilibrium at low temperatures) that it has not been widely used by metallurgists.

Recently, Seltz and co-workers have introduced a greatly improved method for studying alloys by measurement of equilibrium electrode potentials in molten salts.²⁻⁴ The mathematical treatment is the same, of course, as for equilibrium potentials of amalgams in aqueous solutions.⁵ This method will probably find extensive use, since it makes possible not only the determination of phase fields of equilibrium diagrams but also the determination of certain thermodynamic quantities which can be used advantageously in metallurgical calculations. However, the method presents difficulties. With many metallic and alloy electrodes, reversibility is not readily obtainable. Also, the difficulty of obtaining suitable material from which to make the cells is increased as the temperature is increased. Moreover, the necessity of carrying out measurements in a vacuum requires additional apparatus and introduces considerable difficulty, especially at the higher temperatures.

Apparently, no consideration has been given heretofore to the metallurgical use of irreversible electrode potentials that exist when a specimen is immersed in a suitable aqueous solution at room temperature. The apparatus and the method required for such measurements are very simple, and if the results of such measurements could be demonstrated to be reproducible they might be very valuable in studying the structure of alloys. The method would not have the scope of that developed by Seltz and his co-workers because no thermodynamic quantities could be calculated from the data. However, the utility and the simplicity of the method might warrant extensive use for the determination of phase fields and similar applications.

THEORY OF IRREVERSIBLE POTENTIALS

A brief review of the theory of irreversible potentials will be given before showing how to interpret the potential readings in terms of alloy structure. It is known that heterogeneity of a metal surface in an electrolyte will produce points of different potentials, with the result that current flows between these points and electrochemical reactions occur. The points at which oxidation reactions are localized are known as anodes, and those at which reduction reactions are localized are known as cathodes.^{6,7,8} For the benefit of those who are not familiar with the terms anode and cathode as applied to a primary cell, the potential difference between anode and cathode of such a cell can be measured when

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¹ References are at the end of the paper.

the negative terminal of a potentiometer is connected to the anode and the positive terminal is connected to the cathode.

The potentials of anodes and cathodes

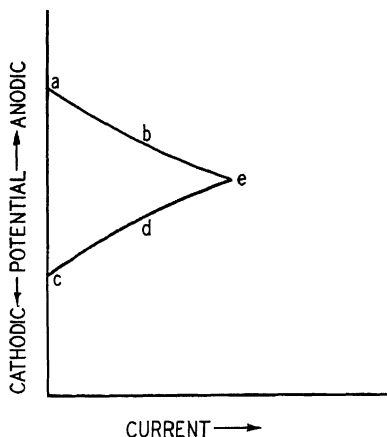


FIG. 1.—SCHEMATIC REPRESENTATION OF POLARIZATION.

vary with the current density on them. The change of the potential of an anode or a cathode resulting from current flow is known as polarization. Polarization is always in such a direction that the potentials of the anode and cathode approach each other as the current through the cell increases. Hence, if the cell is short-circuited, as are local electrodes on a single piece of metal immersed in an electrolyte, the potentials of the anode and cathode are the same. This potential is the one that is measured when a piece of metal, composed of local electrodes, is immersed in an electrolyte.

The relations just described are shown diagrammatically in Fig. 1; a is the potential of the anode and c the potential of the cathode when no current is flowing between them. When current flows, the potential of the anode follows the anodic polarization curve a, b, e and the potential of the cathode follows the cathodic polarization curve c, d, e . The intersection of the curves at point e represents the limiting value of the current. As a result of this polarization, the

potential corresponding to point e exists over the entire surface of the electrode and is, therefore, the potential of the metal measured against some reference electrode.

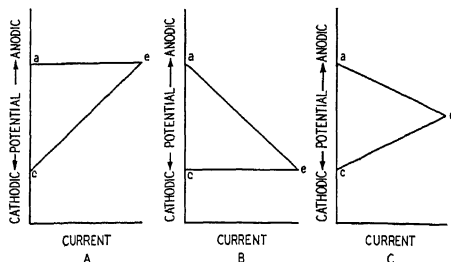


FIG. 2.—THREE TYPES OF POLARIZATION DIAGRAMS (AFTER EVANS).

Obviously, the measured potential may have any value between a and c , depending upon the slope of the polarization curves.⁹⁻¹⁰ The slopes of these polarization curves depend both upon the nature of the electrolyte and the area of anode and cathode. Other variables being constant, the slope of the polarization curve will be inversely proportional to the area of the local elements.¹¹⁻¹² The possible relations are shown schematically in Fig. 2, where the polarization curves are represented by straight lines for simplicity.

Fig. 2A shows the relations that obtain when the anodic area is very large, or when there is little polarization of the anode, even with high current densities, and when the cathodic areas are polarized substantially. In this, the case measured voltage e closely approximates the potential of the anode when no current is flowing. Fig. 2B represents the conditions that obtain when the anodic area is very small, or when there is little polarization of the cathode, even at high current densities. In this case, the measured potential e closely approximates the potential of the cathodic areas when no current is flowing. Fig. 2C represents the conditions that obtain when both cathodic and anodic areas are highly polarized; the measured potential e will have values between the potentials of the anode and cathode.

If the area of the anode phase is small and it is desirable to detect its presence by potential measurements, the amount of anodic polarization should be reduced to a minimum. Conversely, if one desires to detect the presence of a cathode phase, the amount of cathodic polarization should be reduced to a minimum.

DEVELOPMENT OF METHOD

The choice of the solution in which to make the measurement will depend upon the type of polarization desired, and also upon the open-circuit potentials of the local anodes and cathodes. Although the known effect of certain ions on polarization will help in the selection, a satisfactory solution can be obtained only by experiment.

Early in the work on aluminum alloys, it was found that neutral chloride solutions gave more reproducible potentials than did other common electrolytes. However, the time required to reach a steady reading with solutions of neutral chlorides alone was often as long as 24 hr. Also, fluctuations in potential frequently occurred, probably as a result of variations in oxygen content of the solution. It was found that the addition of hydrogen peroxide to the chloride solution minimized these difficulties. This work led to the choice of a solution containing 53 grams of sodium chloride and 3 grams of hydrogen peroxide per liter.

In order to ensure reproducible results, it was necessary that a standard method of surface preparation be developed. Many methods were tried. One of the most reproducible surfaces was obtained by machining, using a very light cut in the final operation. Machining was not adopted for the standard preparation of surfaces, however, because the method was expensive and time-consuming, and because it was difficult to apply to sheet specimens. The method that was selected, and which gave results that were almost as consistent as those of a machined surface, was as follows:

The specimen was first degreased with carbon tetrachloride, then abraded with No. 120 emery paper, and finally abraded slightly with No. 00 steel wool. The steel

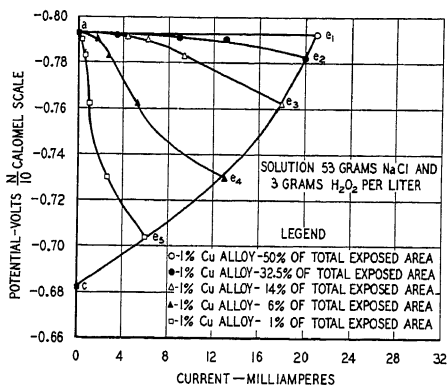


FIG. 3.—EFFECT OF POLARIZATION ON POTENTIAL OF DUPLEX ELECTRODES.

Anodic alloy, 0.97 per cent Cu; cathodic alloy, 4.25 per cent Cu.

wool had sufficient cutting action to remove small particles of emery that were embedded in the surface in the previous operation.

Other features of the method were standardized to assure reproducible results. A 0.10 normal calomel electrode was used as a reference electrode. The potentials were measured on a Leeds and Northrup type K-2 potentiometer. The temperature was held at $25^{\circ} \pm 1^{\circ}\text{C}$.

BINARY ALUMINUM-COPPER ALLOYS

When this method was used, an aluminum-copper solid solution high in copper was found to be cathodic to an aluminum-copper solid solution low in copper. For example, a couple formed by connecting an aluminum-copper solid solution containing 1 per cent Cu through a sensitive milliammeter to an aluminum-copper solid solution containing 4.25 per cent Cu produced a current flowing in the direction that demonstrated that the latter solid solution was cathodic. However, the current flow and the potential of the short-

circuited couple varied with the ratio of exposed electrode areas, as shown in Fig. 3. In this figure polarization curves are shown for anodic electrodes (1 per cent Cu alloy)

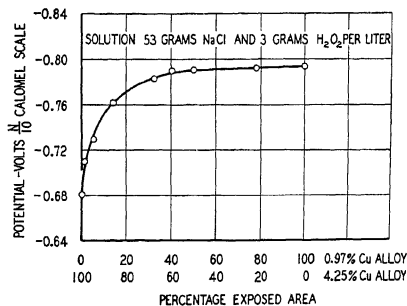


FIG. 4.—POTENTIAL OF ELECTRODES COMPOSED OF TWO ALUMINUM ALLOYS OF DIFFERENT COPPER CONTENTS IN ELECTRICAL CONTACT.

Anodic alloy, 0.97 per cent Cu; cathodic alloy, 4.25 per cent Cu.

of various areas and a polarization curve for a fixed area of the cathodic electrode (4.25 per cent copper alloy). The areas of the anodic electrodes have been expressed as percentages of the total areas of both electrodes exposed to the solution. As would be expected, the anodic polarization decreases as the area of the anode is increased. The intersection of the anodic polarization curves with the cathode polarization curve is the magnitude of current that will be obtained when these anodes of various areas are short-circuited to the cathode. The value of potential at these intersections would be expected to correspond to the measured potential of two-phase alloys composed of various amounts of solid solutions containing 1 per cent and 4.25 per cent Cu, respectively. The potentials at which these curves intersect (e_1 , e_2 , etc.) were plotted against the percentage areas of either electrode exposed to the solution, and the curve shown in Fig. 4 was obtained. This curve shows that as the area of the most anodic alloy (1 per cent Cu) is increased, the potential rises and reaches a value practically equal to the potential of the most anodic alloy.

Also, a large specimen of CuAl_2^* coupled to any one of a series of aluminum-copper solid solutions produced a couple that had the same potential as the same aluminum-copper solid solution that was not connected to the CuAl_2 cathode. As in the case of the couples composed of two aluminum solid solutions of different copper contents, this demonstrates that in the standard solution the cathodic polarization predominates.

Hence the potential of an aluminum-copper alloy would be controlled by the amount of copper that is in solid solution. For example, an aluminum-copper alloy containing 4 per cent Cu but having only 2 per cent Cu in solid solution would have the same potential as a 2 per cent Cu alloy with the copper entirely in solid solution. Also, the potential of an aluminum-copper alloy will be independent of the heat-treating temperature, providing all the copper is in solid solution at all of the heat-treating temperatures. *Therefore, by means of potential measurements in a solution containing 53 grams of sodium chloride and 3 grams of hydrogen peroxide per liter, it should be possible to determine the amount of copper in an aluminum-copper solid solution.*

A series of aluminum-copper alloys in the form of cold-rolled sheet containing from 0 to 7 per cent Cu was heat-treated at five different temperatures for 16 hr. and quenched in cold water. Assuming that a treatment of 16 hr. at these temperatures is sufficient to produce equilibrium, and that the quenching was of sufficient rapidity, the solid solubility at these temperatures was deduced.

The measured potentials of the samples heat-treated at each temperature were plotted against the copper content, and gave a curve with two branches—one a curved line with a pronounced slope, and the other a straight horizontal line. The curves for all temperatures were super-

* The potential of CuAl_2 by itself is -0.53 volts on the 0.1N calomel scale.

imposed as shown in the lower part of Fig. 5.* Since the potential is controlled by the copper content of the solid solution, the curved line indicates a change in copper

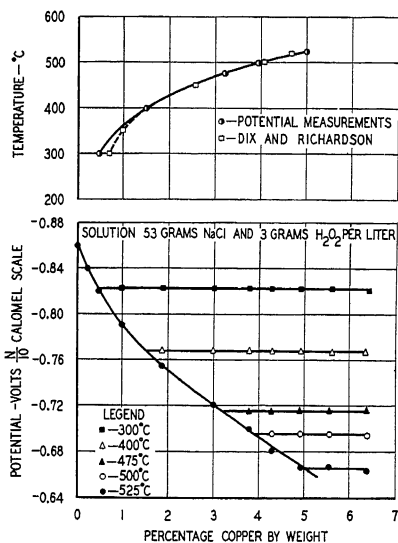


FIG. 5.—POTENTIAL OF BINARY ALUMINUM-COPPER ALLOYS AND THE DERIVED SOLID SOLUBILITY CURVE.

content of the solid solution and the straight line indicates no further change in it; therefore the point of intersection of the two lines clearly shows the limit of solid solubility.

The solubility curve as determined in the lower part of Fig. 5 is plotted in the upper part of the figure in comparison with the curve obtained by Dix and Richardson.¹³ The two curves check very well except at the two lowest temperatures. From the thermodynamics of perfect solutions, it has been shown that a plot of the reciprocal of the absolute temperature against the logarithm of the solid solubility expressed in atomic per cent should be a straight line. The data on the solid solubility of copper in aluminum obtained by potential measurements did fall on a straight line when so plotted.

* On the curved line, only the points obtained at 525°C. are indicated because the points on the curved lines obtained at lower temperatures coincide with those obtained at 525°C.

TERNARY ALLOYS

It should be possible in a like manner to determine the limits of solid solubility and

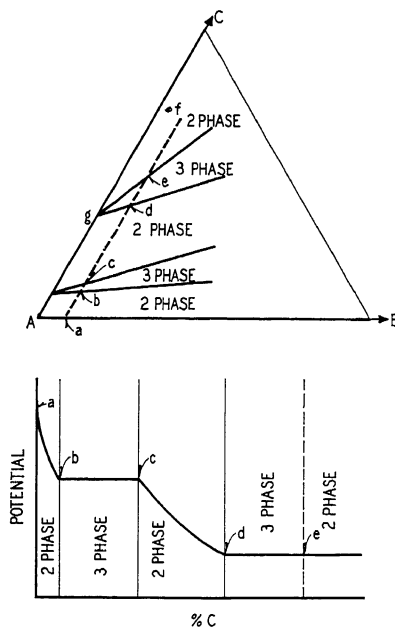


FIG. 6.—POTENTIAL OF SERIES OF ALLOYS ALONG SECTION *a-f* OF HYPOTHETICAL DIAGRAM ABOVE.

some of the phase fields of ternary alloys. In the upper part of Fig. 6 is shown an isothermal section of a hypothetical ternary diagram. In this section of the diagram, element *B* has practically no solid solubility in *A*, whereas *C* has a limited solid solubility, indicated by *g*. If a series of alloys along the section *a-f* behaves in the same manner in an electrolyte as the aluminum-copper alloys did in the hydrogen peroxide-sodium chloride solution, the potential curve shown in the lower half of Fig. 6 should be obtained. From *a* to *b*, the potential will become more cathodic because the amount of *C* in solid solution is increasing. The potential will remain constant for alloys from *b* to *c* because the composition of the solid solution does not change. Beyond *c* and until *d* is reached,

the potential will again become more cathodic because the amount of C in solid solution is increasing. However, beyond d , the potential will not be changed by

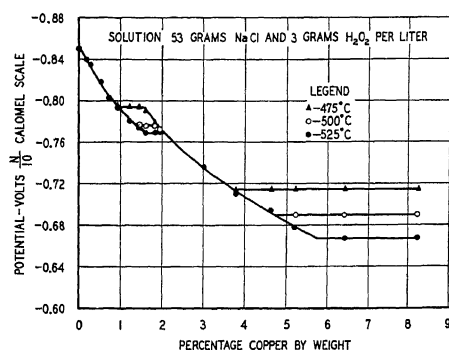


FIG. 7.—POTENTIAL OF SERIES OF ALUMINUM-COPPER ALLOYS CONTAINING 0.35 PER CENT IRON.

further additions of C because the concentration of the solid solution is unchanged.

Aluminum-copper-iron Alloys.—Since iron is practically insoluble in aluminum

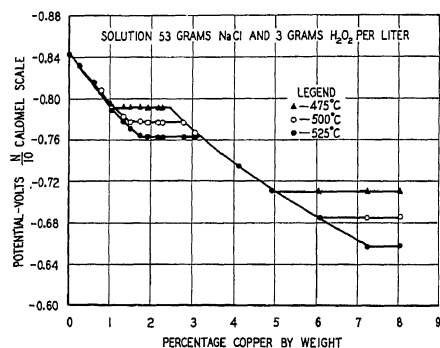


FIG. 8.—POTENTIAL OF SERIES OF ALUMINUM-COPPER ALLOYS CONTAINING ONE PER CENT IRON.

and copper has a limited solubility in aluminum, two series of aluminum-copper-iron alloys were prepared in order to test the relations (described in previous section) between potentials and structure. In Fig. 7 are shown the potentials of a series of aluminum-copper-iron alloys containing 0.35 per cent Fe and from 0 to 8 per cent Cu, which had been heat-treated for 16 hr. at three different temperatures. As for the

binary aluminum-copper alloys, the sheet was in the hard-rolled temper prior to heat-treatment. In Fig. 8 a similar curve is shown for a series of aluminum-copper-iron

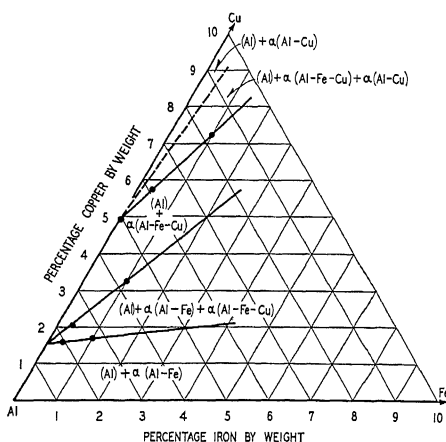


FIG. 9.—ALUMINUM CORNER OF ALUMINUM-COPPER-IRON CONSTITUTIONAL DIAGRAM AT 525°C.

alloys containing 1 per cent Fe and from 0 to 8 per cent Cu. The shape of these experimental curves is similar to those indicated

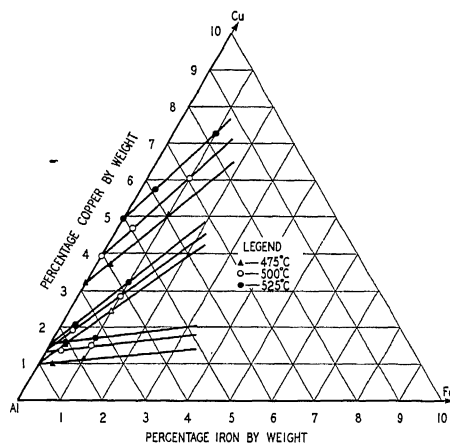


FIG. 10.—EFFECT OF TEMPERATURE ON PHASE BOUNDARIES OF ALUMINUM CORNER OF ALUMINUM-COPPER-IRON SYSTEM.

in Fig. 6. As for the binary aluminum-copper alloys, the curved portions of these diagrams are similar regardless of the heat-

treating temperature. The two horizontal sections are altered by a change in the heat-treating temperature. An isothermal section at 525°C . of the aluminum corner of

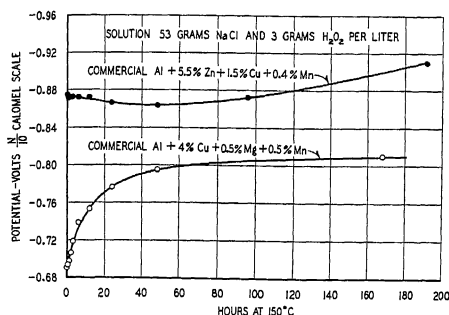


FIG. 11.—ISOTHERMAL DECOMPOSITION OF SUPERSATURATED SOLID SOLUTIONS.

the aluminum-copper-iron constitutional diagram obtained from Figs. 7 and 8 is shown in Fig. 9. This section is consistent with the aluminum corner of the diagram reported by Bradley and Goldschmidt.¹⁴

The employment of a triangular diagram enables the investigator to check the accuracy of his results. For example, a check on the location of the boundary between the two-phase field of aluminum solid solution (Al) and the $\alpha(\text{Al-Fe-Cu})$ constituent; and the three-phase field of aluminum solid solution, $\alpha(\text{Al-Fe-Cu})$ constituent, and $\alpha(\text{Al-Cu})$ constituent can be made in the following manner: A straight line drawn through the points on this boundary for the 1 per cent Fe alloy and the 0.35 per cent Fe alloy should intersect the 0 per cent Fe line at the solid solubility limit of copper in aluminum at the temperature in question. Also, a check may be made on the other two-phase boundaries shown in Fig. 9 in a similar manner. The two lines passing through the points on these boundaries for the 0.35 per cent Fe and the 1 per cent Fe alloys should intersect the 0 per cent Fe line at the same point. This check has been applied to the data obtained from Figs. 7 and 8 and is shown in Fig. 10.

DECOMPOSITION OF SOLID SOLUTIONS

It was found that irreversible potential measurements made at 25°C . can be used to

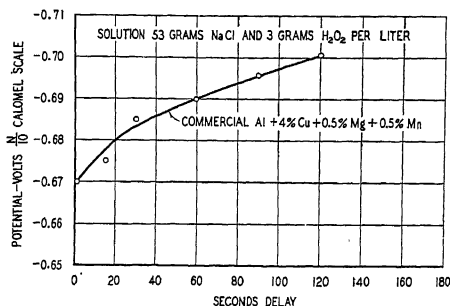


FIG. 12.—DECOMPOSITION OF SOLID SOLUTION CAUSED BY DELAY OF QUENCH.

gain an insight into the mechanism of decomposition of solid solutions. Two examples are shown in Fig. 11. The potential of commercial aluminum containing 4 per cent Cu, 0.5 per cent Mg, and 0.5 per cent Mn was found to become more anodic the longer it was heated at 150°C . This would indicate a gradual decrease in the copper content of the aluminum solid solution at that temperature. On the other hand, commercial aluminum containing 5.5 per cent Zn, 1.5 per cent Cu, and 0.4 per cent Mn showed, first, a potential change in the cathodic direction during the initial period at 150°C ., which was followed by a change in potential in the anodic direction during the subsequent stages. It has been shown that zinc in solid solution alters the potential of aluminum in an anodic direction, whereas copper in solid solution alters the potential in a cathodic direction. Because the potential became more cathodic during the initial stages, it was indicated that the zinc content of the solid solution was decreasing. The subsequent shift of the potential in the opposite direction indicated that the copper content of the solid solution was decreasing after prolonged heating. These results would indicate that the decomposition of such an alloy is at least a two-step phenomenon.

Another example of the decomposition of solid solution is shown in Fig. 12. Specimens (4 by 1 by 0.064 in.) of a commercial aluminum alloy that contained 4 per cent Cu, 0.5 per cent Mg, and 0.5 per cent Mn were heat-treated at 510°C. in a nitrate bath for 15 min., held in air for various periods of time and quenched in cold water, and their potentials were determined. The results show that the longer the specimen was held in air prior to quenching in cold water, the more anodic the potential of the alloy became. This would indicate that the longer the delay before quenching, the less the amount of copper retained in solid solution, or, in other words, the greater the decomposition of the solid solution.

The suitability of this method for determining concentration of solid solution, or the most anodic regions of the solid solution, suggests a number of metallurgical problems in the solution of which irreversible electrode potentials might be very useful. Diffusion studies at once suggest themselves; in fact, the method has already been used to a limited extent for studying the extent of diffusion. Segregation, coring, rate of solution, identification of alloys, determination of porosity in metallic and perhaps other types of coatings, all offer possibilities for the advantageous use of the method described in this paper.

SUMMARY

The electrochemical method described above is being used advantageously in metallurgical investigations of various types, such as solid solubility determinations, diffusion studies, age-hardening problems, determination of phase fields. The basis of the method is the theory of irreversible electrode potentials, which has been explained and expanded. The equipment and technique required are relatively simple, and the measurements can be made with considerable rapidity.

Typical data of this kind have been presented on binary and ternary aluminum-

base alloys, which illustrate the utility of the method.

ACKNOWLEDGMENT

This work was initiated as a result of preliminary unpublished work by Mr. E. I. Dix, Jr. and Dr. L. J. Weber. Mr. D. C. Sprowls made some of the potential measurements. Dr. H. R. Freche checked the identification of the phases in the aluminum-copper-iron system by X-ray diffraction measurements. The author gratefully acknowledges the interest and suggestions by other members of the staff of the Aluminum Research Laboratories.

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DISCUSSION

(C. S. Barrett presiding)

C. H. SAMANS,* State College, Pa.—On page 118 the authors say “. . . it should be possible to determine the amount of copper in an aluminum-copper solid solution.” It would be of interest to ascertain whether the method would be of any value in determining the cause of precipitation-hardening in these alloys—whether it is due primarily to true precipitation or to some pre-precipitation process. It would seem that if the former is true the copper atoms would no longer be in solid solution, hence the

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method should be applicable regardless of the size of the CuAl_2 particles. However, in the latter case the copper atoms presumably would still be part of the solid solution even though they might be concentrated in regions that no longer have its exact symmetry. Would the potentials for the two cases differ?

C. S. BARRETT,* Pittsburgh, Pa.—In drawing conclusions from irreversible potential curves of solid solutions during decomposition, it would seem to be necessary first to eliminate the possible effect of strains on the curves. Is it possible that strains generated in the matrix or in the precipitate during aging could account for any features in the aging curves of Fig. 11?

R. H. BROWN (author's reply).—Answering Professor Samans: The data given in the paper show clearly that precipitation can be determined by potential measurements, provided the precipitation has gone far enough to substantially change the copper concentration of the anodic areas. However, his question undoubtedly refers to the early stages of age-hardening, and during these early stages there would be no significant change in the concentration of copper in anodic areas, regardless of whether the copper particles that obstruct slip are true precipitate or some hypothetical agglomerate. In other words, the method described in the paper would not be expected to detect the early stages of precipitation. This has been borne out by experiment, since we have been unable to determine any change in

heat-treated and quenched duralumin by room-temperature aging.

If a solution were found in which the anode areas would polarize readily and the cathode areas would not polarize at all, there might be some chance of detecting precipitation in the early stages. Even then, however, there is some doubt, because we do not know how much effect on potential would be expected, as copper atoms change from a random distribution (which they are supposed to have in knots and other hypothetical agglomerates) to the ordered arrangement they have in the precipitate. That is, since the potential seems to be mainly dependent upon the concentration of the copper, it is doubtful whether changing from random distribution of copper atoms (knots) to an ordered arrangement of copper atoms (precipitate) would alter the potential measurably; assuming, of course, the same percentage of copper in each case.

In reply to Professor Barrett's question concerning the effect of strains on the measured potential, it would appear that if strains in the alloys are to affect the potential, a solution other than the one used in this investigation will be necessary. In the salt-peroxide solution, high-purity aluminum and aluminum-copper solid solutions, cold-worked to various degrees, were found to have the same potentials as annealed high-purity aluminum and rapidly quenched aluminum-copper solid solutions, respectively.

It should be pointed out that the method is relatively new, and consequently all its limitations, as well as many of its useful applications, have not been found.

* Metals Research Laboratory, Carnegie Institute of Technology.

X-ray Study of the Solid Solubility of Lead, Bismuth and Gold in Magnesium

BY FRANK FOOTE* AND E. R. JETTE,† MEMBERS A.I.M.E.

(Cleveland Meeting, October 1940)

PRECISION lattice-constant measurements have been widely used in the study of cubic solid solutions but as yet have been rarely applied to noncubic solid solutions. (See, however, references 1 and 2.) With the high precision at present attainable in the measurement of lattice constants, the X-ray method should be readily applicable to noncubic solid solutions. In the work reported here, hexagonal close-packed magnesium was used as the solvent and either lead, bismuth or gold as the solute. In the magnesium-lead and magnesium-bismuth systems the a and c lattice constants were determined as a function of composition, densities were calculated from these lattice-constant data, these theoretical densities were compared with those directly measured and the solid solubility limit was determined on quenched specimens over a considerable range of temperature. In the magnesium-gold system, the solid solubility is very small but we have obtained an indirect check on the solubility limit previously reported.

MATERIALS AND PREPARATION OF THE ALLOYS

The magnesium used was obtained from the Aluminum Company of America and was 99.987 per cent pure. Impurities as reported on the label were: Fe, Al, 0.004

per cent; Si, 0.009 per cent; Zn, trace; Cu, Pb, nil. The bismuth was Merck's analytical grade, minimum purity 99.95 per cent. Maximum impurities as listed on the label were: Fe, 0.008 per cent; Pb, 0.010 per cent; Ag, 0.010 per cent; Cu, 0.005 per cent; Sn, 0.003 per cent; Sb, 0.00; As, 0.000; S, 0.01 per cent. The gold was purified by double precipitation with sulphur dioxide. The lattice constants of these three metals have been previously reported.³ The lead used was test lead, silver free and with a maximum of 0.10 per cent heavy metal impurities. The lattice constant of this lead has been measured and found to be 4.94057 ± 0.00018 at 25°C .

The alloys were prepared by melting together weighed amounts of the constituent metals in magnesia-lined alundum crucibles under an atmosphere of hydrogen purified by passing over magnesium heated to 500°C . The magnesia lining prevented contamination of the alloys with aluminum. Vacuum melting could not be used because of the volatility of magnesium. A high-frequency induction furnace was used for the melting operation and the stirring action of the current resulted in thorough mixing of the constituents. The melts were allowed to freeze in the crucible, the ingots obtained weighed about 10 grams. An extremely thin white film formed on the surface of the melts, sometimes covering only a part of the exposed surface. The ingots were filed clean, placed in small iron crucibles with close-fitting lids and individually sealed into Pyrex glass tubes. Before sealing off, the tubes were alter-

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¹ References are at the end of the paper.

nately evacuated and filled with pure hydrogen a number of times to displace air. Finally hydrogen was admitted to a pressure of approximately half an atmosphere and the tube was sealed off. The ingots were annealed for at least a week at temperatures close to the eutectic temperature. This technique hinders the transfer of magnesium from the alloy to the glass container; the iron crucible prevents direct contact between the alloy and the glass, the hydrogen retards the diffusion of magnesium vapor. The alloys were then quenched in water and again cleaned by filing. The ingots were preserved in a desiccator.

LATTICE-CONSTANT MEASUREMENTS

Samples for X-ray analysis were prepared by filing. Two techniques were used in heat-treating these filings. For annealings below 400°C., the samples were sealed into evacuated glass tubes. At temperatures above 400°C. these high-magnesium alloys rapidly attack glass, and films from such samples often showed diffuse lines. For many of these higher-temperature anneals the filings were packed into small thin-walled iron crucibles with loosely fitting lids. These crucibles were then sealed into glass tubes. The samples were annealed for various periods of time at suitable temperatures in vertical rapid quenching furnaces. The samples were quenched by crushing the tubes under butyl acetate. A number of analyses showed no increase in iron content during this treatment.

The general X-ray technique has been previously described.³ The K_{α} radiations from an iron target were used, the wave lengths were taken from the second edition of Siegbaum's book.⁴ Five doublets were measured on each film. Correction for the index of refraction was applied and the lattice constants calculated by the method of Cohen.^{5,3} All lattice constants were reduced to a common temperature of 25°C., using the expansion coefficients for

magnesium as given by Raynor and Hume-Rothery.⁶

Many of these alloys are rapidly attacked by water or moist air, particularly with the sample in the form of filings. In dry air the alloys are stable, the ingots kept in a desiccator remained bright and clean indefinitely. To minimize the effect of water and water vapor, the alloy filings were quenched in a nonaqueous liquid and the work was carried out during the cold winter months when the water-vapor content of the atmosphere was low. The mounted samples for X-ray exposure were prepared with Duco cement and a thin smear of the cement was placed over the sample. During the exposure, therefore, the filings were embedded in Duco cement and were not in direct contact with the atmosphere. The powders remained bright throughout the exposure. In all cases, sharp diffraction lines, indicating uniformity of composition, were obtained.

DENSITY MEASUREMENTS

Density measurements were made on many of the annealed single-phase alloys. The loss-of-weight method was employed, using monobrombenzene as the density liquid. This method has been previously described.⁷ The density samples were annealed and quenched filings, millings or small chips. No reaction between the alloys and the monobrombenzene was observed; the samples remained clean and bright throughout the determinations.

CHEMICAL ANALYSIS

The alloys were analyzed for lead, bismuth or gold following the methods given in Hillebrand and Lundell.⁸ Lead was determined as PbO_2 by electrolysis, bismuth as $BiOCl$ and gold as free metal by precipitation with sulphur dioxide. The methods were checked by analysis of solutions containing large amounts of magnesium and known amounts of the second metal. Unless otherwise indicated, the analyses

were made on a portion of the annealed filings used for the X-ray analysis. The density samples were analyzed after the density measurements were completed, the whole

weight of the alloy and V' the volume of the unit cell in terms of cubic Crystal Ångströms (1 Crystal Ångstrom = 1 Å_{cr} = 10³ (× units)). The quantity $K = 10^{24}/f^3N$

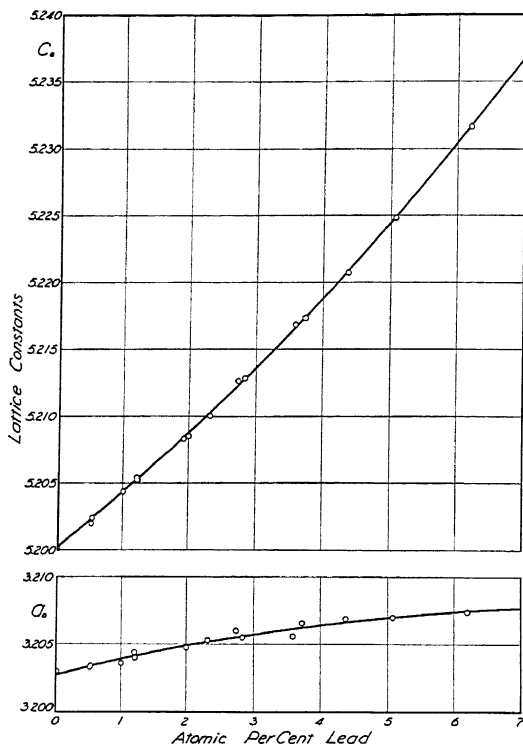


FIG. 1.—LATTICE CONSTANTS OF SINGLE-PHASE MAGNESIUM-LEAD ALLOYS.

sample being used for this analysis. All compositions were converted to atomic per cent, using for the atomic weights: Mg, 24.32; Pb, 207.21; Bi, 209.00; Au, 197.2.

CALCULATION OF THEORETICAL DENSITY

Jette and Foote⁹ have shown that the theoretical density should be calculated from lattice-constant data by means of the following formula:

$$\rho = \frac{10^{24}}{f^3N} \frac{nM}{V'} = K \frac{nM}{V'} \quad [1]$$

where N is Avogadro's number, f the ratio between the absolute and the relative scale of X-ray wave lengths, n the number of atoms per unit cell, M the average atomic

weight of the alloy and V' the volume of the unit cell in terms of cubic Crystal Ångströms (1 Crystal Ångstrom = 1 Å_{cr} = 10³ (× units)). The quantity $K = 10^{24}/f^3N$ has been evaluated from published data on calcite and was found to have a numerical value of 1.65023.⁹ Magnesium has a hexagonal close-packed structure, contains two atoms per unit cell and the volume of the unit cell can be calculated from the a and c lattice constants by the equation $V' = \frac{1}{2}\sqrt{3}a^2c$. Introducing these constants into equation 1, our density formula becomes:

$$\begin{aligned} \rho &= \frac{1.65023 \cdot 2 \cdot 2}{\sqrt{3}} \times \frac{M}{a^2c} \\ &= 3.81104 \times \frac{M}{a^2c} \text{ grams/cu. cm.} \quad [1'] \end{aligned}$$

It should be emphasized that in equation 1' the value of M depends upon the type

of solid solution assumed and that a and c are expressed in terms of "Crystal Ångströms."

LATTICE CONSTANTS AND DENSITIES OF THE
SINGLE-PHASE MAGNESIUM-LEAD AND
MAGNESIUM-BISMUTH ALLOYS

The lattice-constant data for the single-phase magnesium-lead alloys are tabulated in Table 1 and plotted in Fig. 1. Similar

the compositions were obtained by analysis of a portion of the annealed sample used for the X-ray analysis. The average standard error of the a lattice constants was 0.00020, for the c lattice constants 0.00017 and for the ratio c/a , 0.00012. Both lattice constants increase with increasing alloy content, the a constant slowly, the c constant much more rapidly. Hence, the c/a ratio increases with increasing solute

TABLE 1.—*Single-phase Magnesium-lead Alloys*

| Alloy | Heat Treatment | | At. Per Cent Pb (Analysis) | Lattice Constants (25°C.) | | |
|------------------------|----------------|----------|----------------------------------|---------------------------|---------------------|---------------------|
| | Hours | Deg. C. | | a | c | c/a |
| Mg..... | (Average of 6) | (Ref. 3) | 0 00 | 3.2030 ₀ | 5.2002 ₁ | 1.6235 ₄ |
| 15..... | 3 | 403 | 0.51 | 3.2033 ₀ | 5.2019 ₉ | 1.6239 ₄ |
| 15g ^a | 119 | 410 | 0.53 | 3.2033 ₈ | 5.2023 ₆ | 1.6240 ₅ |
| 18..... | 5 | 418 | 1.00 | 3.2036 ₀ | 5.2043 ₆ | 1.6245 ₂ |
| 14..... | 3 | 403 | 1.21 | 3.2044 ₀ | 5.2053 ₉ | 1.6244 ₄ |
| 14g..... | 119 | 410 | 1.21 | 3.2040 ₇ | 5.2052 ₆ | 1.6246 ₄ |
| 11..... | 5 | 439 | 1.93 | 3.2046 ₂ | 5.2082 ₃ | 1.6252 ₀ |
| 11g..... | 117 | 400 | 2.00 | 3.2047 ₂ | 5.2085 ₇ | 1.6252 ₄ |
| 19..... | 5 | 448 | 2.32 | 3.2052 ₂ | 5.2100 ₂ | 1.6254 ₅ |
| 10..... | 3 | 438 | 2.73 | 3.2060 ₀ | 5.2125 ₁ | 1.6258 ₅ |
| 10g..... | 117 | 400 | 2.84 | 3.2052 ₂ | 5.2127 ₇ | 1.6261 ₈ |
| 13..... | 4.5 | 450 | 3.59 | 3.2056 ₂ | 5.2168 ₉ | 1.6274 ₉ |
| 12g..... | 118 | 400 | 3.73 | 3.2066 ₂ | 5.2172 ₅ | 1.6270 ₁ |
| 20..... | 6 | 449 | 4.37 | 3.2068 ₄ | 5.2200 ₉ | 1.6279 ₃ |
| 16..... | 4.5 | 448 | 5.07 | 3.2069 ₈ | 5.2247 ₉ | 1.6291 ₀ |
| 17..... | 4.5 | 448 | 6.20 | 3.2074 ₄ | 5.2316 ₃ | 1.6310 ₉ |

^a Samples marked g were annealed in glass tubes, all others were annealed in iron crucibles.

TABLE 2.—*Single-phase Magnesium-bismuth Alloys*

| Alloy | Heat Treatment | | At. Per Cent Bi (Analysis) | Lattice Constants (25°C.) | | |
|---------|----------------|----------|----------------------------------|---------------------------|---------------------|---------------------|
| | Hours | Deg. C. | | a | c | c/a |
| Mg..... | (Average of 6) | (Ref. 3) | 0.00 | 3.2030 ₀ | 5.2002 ₁ | 1.6235 ₄ |
| 20..... | 1.0 | 556 | 0.24 | 3.2032 ₀ | 5.2018 ₇ | 1.6239 ₄ |
| 20..... | 0.5 | 536 | (0.25) ^a | 3.2032 ₅ | 5.2017 ₇ | 1.6239 ₀ |
| 20..... | 0.5 | 536 | (0.25) | 3.2034 ₂ | 5.2018 ₀ | 1.6238 ₈ |
| 24..... | 1.0 | 547 | 0.46 | 3.2036 ₀ | 5.2035 ₈ | 1.6242 ₂ |
| 21..... | 0.5 | 536 | (0.50) | 3.2042 ₇ | 5.2042 ₇ | 1.6241 ₇ |
| 21..... | 0.5 | 536 | (0.50) | 3.2042 ₂ | 5.2042 ₀ | 1.6241 ₇ |
| 25..... | 1.0 | 541 | 0.57 | 3.2035 ₅ | 5.2045 ₂ | 1.6246 ₁ |
| 25..... | 1.0 | 547 | 0.58 | 3.2034 ₂ | 5.2047 ₃ | 1.6247 ₄ |
| 22..... | 0.5 | 532 | (0.76) | 3.2049 ₅ | 5.2060 ₂ | 1.6243 ₇ |
| 22..... | 0.5 | 532 | (0.76) | 3.2045 ₂ | 5.2058 ₆ | 1.6245 ₅ |
| 22..... | 1.0 | 547 | 0.80 | 3.2041 ₂ | 5.2059 ₂ | 1.6247 ₆ |
| 22..... | 1.0 | 541 | 0.81 | 3.2042 ₈ | 5.2058 ₅ | 1.6246 ₆ |
| 15..... | 2.0 | 550 | (1.00) | 3.2043 ₁ | 5.2072 ₅ | 1.6250 ₈ |
| 15..... | 2.0 | 553 | 1.00 | 3.2042 ₈ | 5.2073 ₅ | 1.6251 ₂ |
| 15..... | 1.0 | 548 | 1.01 | 3.2052 ₆ | 5.2074 ₉ | 1.6256 ₇ |

^a Analyses in parentheses are ingot analyses.

data for the magnesium-bismuth alloys are tabulated in Table 2 and plotted in Fig. 2. The heat-treatments refer to the final powder anneals. Unless otherwise stated,

content and approaches but does not reach the theoretical value of 1.633 for hexagonal close-packed spheres. Raynor¹ found this same effect in the Mg-Ag, Mg-Ga and

Mg-In systems. There are large negative deviations from Vegard's rule for the additivity of atomic volumes. The lattice constants as a function of composition can

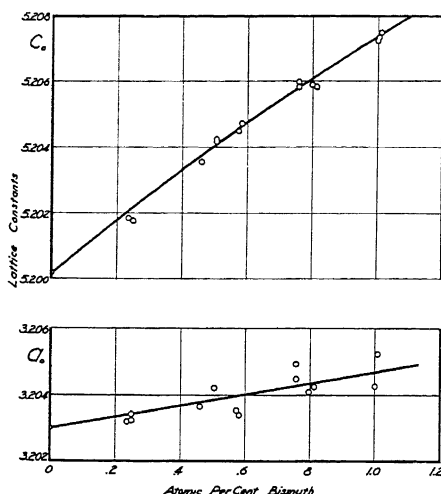


FIG. 2.—LATTICE CONSTANTS OF SINGLE-PHASE MAGNESIUM-BISMUTH ALLOYS.

be satisfactorily represented by the least-squares equations:

$$\text{Mg-Pb } a = 3.20292 + 0.001104 (\text{at. \% Pb}) - 0.000060 (\text{at. \% Pb})^2 \quad [2]$$

with an average deviation of $0.00018 A_{\text{cr}}$ or 0.23 at. per cent Pb.

$$c = 5.20020 + 0.003902 (\text{at. \% Pb}) + 0.000188 (\text{at. \% Pb})^2 \quad [3]$$

TABLE 3.—Comparison of Calculated and Measured Densities

| Alloy | At. Per Cent Pb | ρ (25°C.) (Calculated) | ρ (25°C.) (Measured) | $\Delta\rho$ |
|---------|-----------------|-----------------------------|---------------------------|--------------|
| Mg..... | 0.00 | 1.737 | 1.736 | -0.001 |
| 15..... | 0.60 | 1.815 | 1.807 | -0.008 |
| 18..... | 1.04 | 1.870 | 1.866 | -0.004 |
| 14..... | 1.24 | 1.896 | 1.888 | -0.008 |
| 19..... | 2.36 | 2.038 | 2.039 | +0.001 |
| 20..... | 4.25 | 2.279 | 2.277 | -0.002 |
| 16..... | 5.07 | 2.382 | 2.376 | -0.006 |
| 17..... | 6.26 | 2.532 | 2.527 | -0.005 |
| | At. Per Cent Bi | | | |
| Mg..... | 0.00 | 1.7373 | 1.7362 | -0.0011 |
| 20..... | 0.25 | 1.7689 | 1.7666 | -0.0023 |
| 24..... | 0.46 | 1.7954 | 1.7921 | -0.0033 |
| 25..... | 0.58 | 1.8107 | 1.8063 | -0.0044 |
| 25..... | 0.60 | 1.8141 | 1.8141 | 0.0000 |
| 22..... | 0.78 | 1.8367 | 1.8370 | +0.0003 |
| 26..... | 0.95 | 1.8581 | 1.8584 | +0.0003 |

with an average deviation of $0.00010 A_{\text{cr}}$ or 0.022 at. per cent Pb.

$$\text{Mg-Bi } a = 3.20298 + 0.001702 (\text{at. \% Bi}) \quad [4]$$

with an average deviation of $0.00023 A_{\text{cr}}$ or 0.14 at. per cent Bi.

$$c = 5.20015 + 0.008310 (\text{at. \% Bi}) - 0.001131 (\text{at. \% Bi})^2 \quad [5]$$

with an average deviation of $0.00016 A_{\text{cr}}$ or 0.019 at. per cent Bi.

Theoretical densities can be calculated from these lattice-constant data by equa-

TABLE 4.—Two-phase Magnesium-lead Alloys

| Alloy | Alloy Compositions, At. Per Cent Pb | Heat Treatment | | Lattice Constants (25°C.) | | Solubility Limit, At. Per Cent Pb (Eq. 3) |
|------------------|-------------------------------------|----------------|---------|---------------------------|---------------------|---|
| | | Hours | Deg. C. | a | c | |
| 8 | 7.3 | 5.5 | 463 | 3.2099 ₃ | 5.2345 ₉ | 6.67 |
| 8 | 7.3 | 4.5 | 450 | 3.2077 ₅ | 5.2320 ₁ | 6.36 |
| 8 | 7.3 | 5 | 438 | 3.2076 ₅ | 5.2316 ₀ | 6.20 |
| 8 | 7.3 | 5 | 438 | 3.2077 ₆ | 5.2313 ₀ | 6.15 |
| 17 | 6.2 | 6 | 402 | 3.2071 ₄ | 5.2253 ₇ | 5.17 |
| 8 | 7.3 | 5 | 392 | 3.2064 ₃ | 5.2233 ₉ | 4.83 |
| 16 | 5.1 | 122 | 345 | 3.2055 ₂ | 5.2167 ₉ | 3.62 |
| 13g ^a | 3.6 | 501 | 300 | 3.2051 ₇ | 5.2113 ₄ | 2.55 |
| 10g | 2.7 | 506 | 300 | 3.2054 ₂ | 5.2113 ₄ | 2.55 |
| 11g | 1.9 | 736 | 257 | 3.2041 ₉ | 5.2073 ₆ | 1.70 |
| 14g | 1.2 | 736 | 198 | 3.2041 ₁ | 5.2039 ₃ | 0.92 |
| 14g | 1.2 | 5516 | 152 | 3.2033 ₅ | 5.2021 ₉ | 0.50 |

^a Samples marked g were annealed in glass tubes, all others were annealed in iron crucibles.

tion 1'. The calculation has been made on the assumption of simple substitution of lead or bismuth atoms for magnesium

Table 3 gives the comparison between directly measured and calculated densities. The uncertainty in the calculated densities

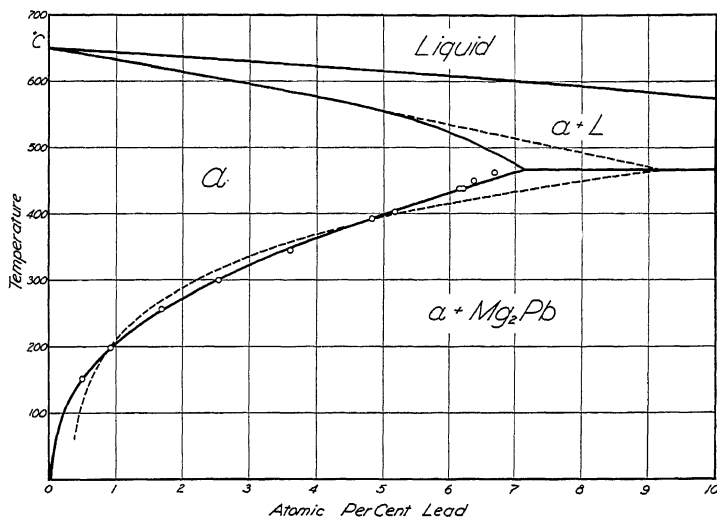


FIG. 3.—PHASE DIAGRAM OF MAGNESIUM-RICH MAGNESIUM-LEAD ALLOYS. Dashed line shows solid solubility limit obtained by Vosskühler.¹²

atoms in the magnesium lattice. On this basis, M is given by:

$$\text{For Mg-Pb, } M = 24.32 + 1.829 \text{ (at. \% Pb)} \quad [6]$$

$$\text{For Mg-Bi, } M = 24.32 + 1.8468 \text{ (at. \% Bi)} \quad [7]$$

is slightly less than 0.001 density unit, the greater part being derived from the uncertainty in the atomic weight of magnesium (and the accidental error of the analysis). The uncertainty in the directly measured densities is slightly greater than 0.001 density unit, assuming that the uncertainty

TABLE 5.—Two-phase Magnesium-bismuth Alloys

| Alloy | Alloy Compositions, At. Per Cent Bi | Heat Treatment | | Lattice Constants (25°C.) | | Solubility Limit, At. Per Cent Bi (Eq. 5) |
|------------------|-------------------------------------|----------------|---------|---------------------------|---------------------|---|
| | | Hours | Deg. C. | a | c | |
| 16 | 2.00 | 1.0 | 548 | 3.2049 ₅ | 5.2077 ₃ | 1.07 |
| 23 | 1.28 | 1.0 | 548 | 3.2049 ₅ | 5.2076 ₃ | 1.05 |
| 23 | 1.28 | 0.5 | 544 | 3.2048 ₃ | 5.2076 ₃ | 1.05 |
| 23 | 1.28 | 0.5 | 544 | 3.2044 ₆ | 5.2079 ₁ | 1.10 |
| 15 | 1.00 | 1.0 | 542 | 3.2045 ₄ | 5.2071 ₂ | 0.97 |
| 23 | 1.28 | 1.0 | 540 | 3.2042 ₅ | 5.2074 ₃ | 1.02 |
| 23 | 1.28 | 0.5 | 538 | 3.2045 ₅ | 5.2073 ₀ | 1.00 |
| 18 | 3.93 | 2.5 | 538 | 3.2041 ₇ | 5.2064 ₄ | 0.86 |
| 15 | 1.00 | 1.5 | 524 | 3.2045 ₅ | 5.2059 ₈ | 0.79 |
| 22 | 0.75 | 2.0 | 493 | 3.2043 ₈ | 5.2046 ₂ | 0.58 |
| 16 | 2.00 | 1.0 | 491 | 3.2043 ₀ | 5.2045 ₀ | 0.57 |
| 17 | 3.00 | 1.0 | 489 | 3.2035 ₇ | 5.2043 ₅ | 0.55 |
| 16 | 2.00 | 2.0 | 453 | 3.2033 ₂ | 5.2029 ₁ | 0.35 |
| 17 | 3.00 | 3.0 | 453 | 3.2032 ₃ | 5.2028 ₇ | 0.34 |
| 22 | 0.75 | 8.0 | 448 | 3.2032 ₇ | 5.2027 ₉ | 0.33 |
| 24 | 0.45 | 35 | 425 | 3.2030 ₈ | 5.2021 ₃ | 0.25 |
| 16 | 2.00 | 119 | 362 | 3.2026 ₇ | 5.2012 ₁ | 0.13 |
| 15 | 1.00 | 119 | 362 | 3.2029 ₆ | 5.2010 ₉ | 0.12 |
| 15g ^a | 1.00 | 5497 | 307 | 3.2028 ₂ | 5.2004 ₃ | 0.03 |
| 16g | 2.00 | 5497 | 307 | 3.2030 ₁ | 5.2005 ₆ | 0.05 |

^a Samples marked g were annealed in glass tubes, all others were annealed in iron crucibles.

in each weighing is 0.0001 gram. The combined uncertainty is approximately 0.002 density units. In some cases the difference between directly measured and

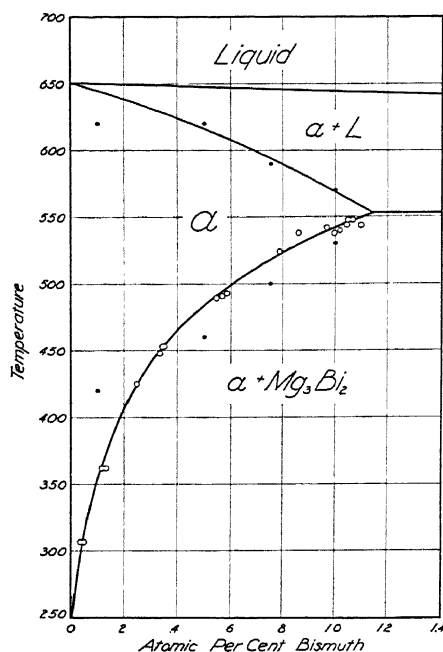


FIG. 4.—PHASE DIAGRAM OF MAGNESIUM-RICH MAGNESIUM-BISMUTH ALLOYS.

Solid circles indicate four points obtained by Grube, Mohr and Bornhak¹⁷ on curve of solid solubility limit.

calculated densities exceeds this combined uncertainty. In all cases of this kind the measured density is lower than the calculated value and the lowered density can be ascribed to physical inhomogeneity; i.e., to the presence of cracks, blowholes, porosity, or other fault. However, the agreement is considered to be sufficiently good to establish the fact that both of these high-magnesium solid solutions are of the simple substitutional type.

Tables 4 and 5 give the lattice-constant data on two-phase alloys and the solid solubility limits calculated from these data. The solubility limits were obtained by substituting the measured lattice-constant values in equations 2, 3, 4 or 5 and solving

for atomic per cent Pb or at. per cent Bi. Since the a lattice constant changes only slightly with composition, the solubility limits obtained from equations 2 and 4 are not very accurate. The limits obtained from the c lattice constants (equations 3 and 5) are considerably more reliable. We have tabulated only the solubility limit values as obtained from the c lattice constants. In general the limits obtained from the a constants confirm the reported solubility limits, but are scattered in a band on both sides of the lines shown in Figs. 3 and 4.

The solubility limit of lead in magnesium has been plotted in Fig. 3. Also plotted in Fig. 3 are the liquidus as drawn through the thermal points obtained by Grube,¹⁰ Kurnakow and Stepanow¹¹ and Vosskühler;¹² the solidus as obtained by Vosskühler¹² from temperature-resistance measurements; and the solid solubility limit (dashed line) as obtained by Vosskühler¹² from conductivity and from temperature-resistance measurements. The eutectic temperature was taken as 468°C., the average of the four previously reported values: 460°C.,¹⁰ 466°C.,¹² 470°C.¹³ and 475°C.¹¹

Hansen^{14,15} has reported a few microscopic observations on the solid solubility limit. His alloys were given short-time anneals (48 hr.) and his results were not conclusive.

Our solid solubility limit agrees reasonably well with that of Vosskühler's¹² up to about 400°C. In this temperature the maximum difference between the two sets of results is approximately 0.3 at. per cent Pb, or 15°C. Above 400°C., the differences are much greater, reaching about 2.1 at. per cent Pb at the eutectic temperature. It is in this temperature region that the results of conductivity and temperature-resistance measurements are least reliable (see Vosskühler's Figs. 2 and 3). In this same region, our c lattice constant is changing most rapidly with composition; that is, it is in this region that

errors in measuring lattice constants have the least effect on the solubility limit. Further, our alloy No. 8, containing 7.3 at. per cent Pb and quenched from 450° and 463°C., is definitely two-phase. We believe, therefore, that our X-ray results are more reliable than those obtained by conductivity methods.

The solubility limit of bismuth in magnesium has been plotted in Fig. 4. Also plotted in Fig. 4 are the liquidus as drawn through the thermal points of Grube¹⁶ and Grube, Mohr and Bornhak;¹⁷ the solidus as determined by Grube, Mohr and Bornhak¹⁷ from temperature-resistance measurements. The eutectic temperature was taken as 553°C.^{16,17}

Grube, Mohr and Bornhak¹⁷ obtained four points on the curve of solid solubility limit. These points are shown on Fig. 4 as solid circles. All of these points are within 0.15 at. per cent Bi of the curve drawn through our results.

TABLE 6.—Summary of Solubility Limit, Lead and Bismuth in Magnesium

| <i>t</i> , Deg. C. | At. Per Cent Pb | Wt. Per Cent Pb | At. Per Cent Bi | Wt. Per Cent Bi |
|-----------------------|--------------------|--------------------|--------------------|--------------------|
| 553 ^a | | | 1.15 | 0.05 |
| 525 | | | 0.81 | 0.56 |
| 500 | | | 0.60 | 4.95 |
| 468 ^a | 7.16 | 39.6 | | |
| 450 | 6.54 | 37.5 | 0.34 | 2.81 |
| 400 | 4.99 | 30.9 | 0.18 | 1.53 |
| 350 | 3.64 | 24.3 | 0.09 | 0.79 |
| 300 | 2.51 | 18.0 | 0.04 | 0.33 |
| 250 | 1.61 | 12.3 | 0.01 ^b | 0.10 ^b |
| 200 | 0.95 | 7.5 | | |
| 150 | 0.49 | 4.0 | | |
| 100 | 0.21 ^b | 1.8 ^b | | |

^a Eutectic temperature.

^b Extrapolated value.

Table 6 gives a summary of the solid solubility limits of lead and bismuth in magnesium. These values were read from large-scale plots.

Magnesium-gold Alloys

Hume-Rothery and Butchers¹⁸ have shown by microscopic methods that the solubility of gold in solid magnesium is approximately 0.1 at. per cent at the

eutectic temperature. This slight solubility makes the establishment of a lattice-constant composition curve difficult. An alloy containing 3 at. per cent Au was annealed 4 hr. at 560°C. and quenched. The alloy was two-phase, the lattice constants of the magnesium-rich phase were found to be: $a = 3.20216$, $c = 5.19924$ at 25°C. Gold in solid solution in magnesium decreases both lattice constants, a by 0.00084 and c by 0.00097 Å_{cr}. These changes in lattice constants are consistent with a solid solubility of approximately 0.1 at. per cent Au as found by Hume-Rothery and Butchers.¹⁸ This conclusion was reached by an indirect method; further work is planned.

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DISCUSSION

(P. H. Brace presiding)

G. EDMUNDS* AND M. L. FULLER,* Palmer-ton, Pa.—We disagree with the opening statement made by the authors that precision lattice measurements have been rarely applied to noncubic solid solutions. This statement is readily refuted by the literature on the subject; e.g., see reference 15, which refers to numerous

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publications giving lattice-parameter determinations on noncubic metals significant to four and more figures.

For the determination of solid solubilities in some alloy systems, very much more precise measurements are needed than in others to obtain a given accuracy. In any case proper specimen preparation and analyses are essential, as has been recognized in the present work.

Lattice constants are reported in the paper to six figures, the sixth figure being given in subscript position. This creates the impression that the lattice constants are correct to five figures. We suggest that five figures would have been adequate, since the standard errors calculated by the authors from each X-ray photogram average two units in the fifth figure. That the accuracy claimed is too high becomes more obvious from an inspection of the curves of Fig. 2. The curves of that figure show the variation of the lattice constants a and c with composition. The a values deviate widely from the curve—this deviation amounting to as much as six units in the fifth figure of the value of a . Less deviation is noted for the c values. The authors do not explain this difference in the accuracy of a and c . If the a values are inaccurate, and since both a and c are calculated from the same original diffraction-line measurements, how reliable are the c values?

It seems that the accuracies of the lattice constants of the magnesium-bismuth alloys and the values of calculated densities and solid solubilities derived therefrom are open to serious doubt, because of the striking lack of conformity to a smooth curve of the values of Fig. 2. Because the a values are squared, errors in them have a larger effect on calculated densities than do errors in c values.

F. FOOTE AND E. R. JETTE (authors' reply).—We believe that our introductory statement is essentially correct. We do not consider that any lattice-constant measurement may claim accuracy of more than four significant figures unless the systematic errors have been removed. These ordinarily are considerably larger than the accidental errors. While methods of eliminating systematic errors for cubic systems have been well known for many years, no really satisfactory method for noncubic systems was

published prior to 1935 (ref. 5), the year Hanson (ref. 15) was printed. Unless the "drift" (cf. refs. 5 and 3) is accounted for, the fifth significant figure is highly uncertain and sometimes even the fourth.

The vexing question of just how many figures should be carried in stating a result still lacks a completely satisfactory answer. It should be noted that the errors quoted are "standard errors," which may be from 50 to several hundred per cent greater than the ordinary "probable errors." In some of our earlier articles an even more conservative estimate of the accuracy of our measurements was used; namely, a fiduciary limit (ref. 3). It is to be emphasized that the standard errors in a and c was calculated from the actual measurements and not merely estimated by some scheme such as taking the error in the line position as ± 0.05 mm. Such standard errors carry the correction factor for the number of observations made; i.e., the number of line pairs on each film. Such care and conservatism in stating the errors of lattice-constant measurements is ordinarily unnecessary and, accordingly, most authors do not use such methods. In any critical comparison of measurements from different sources, the method used in calculating the errors is nearly as important as the method of making the measurement itself. Since the conversion from one method of stating errors to another involves more significant figures than would be required in the simple rules, based in turn on probable errors, we have adopted the form used in these articles. It is clear and should lead to no misunderstanding.

The wave lengths used for the lattice-constant measurements were chosen so as to give lines suitable for the accurate evaluation of the c constants. This procedure is entirely justified by the facts that: (1) the constant that changes the more rapidly with composition is obviously the proper one to use for determining solubility limits (Figs. 1 and 2 show that c changes much more rapidly than a), and (2) the error in the density contributed by the a constants is small compared with that due to the uncertainties in atomic weights (see below). The conditions that must be satisfied to obtain equal percentage errors in a and c were given in ref. 3. For the reasons given above, they were deliberately violated so as to favor a higher accuracy for c .

The error in the calculated densities is correctly stated; the methods used in the calculation are completely covered in ref. 9. The error due to uncertainties in the lattice constant are negligible in comparison with those due to uncertainty in the atomic weights. The average lattice-constant errors could be at least twice as large as they are and in no case would the errors in the calculated density be as great as that contributed by the uncertainty in the atomic weights, the latter uncertainty being taken as plus or minus one unit in the last

quoted figure for the atomic weight as given in the official table for 1940 (cf. ref. 9).

The points on the solubility curve are affected not only by the errors in measuring the lattice constants but also by the degree of completeness with which equilibrium was reached during annealing and by retention of this state during quenching. This discussion of the errors and the "fit" of the points in the solubility curves (Figs. 3 and 4) should answer any questions as to the accuracy of these curves.

Mechanism of Precipitation from the Solid Solution of Silver in Aluminum

BY C. S. BARRETT,* MEMBER, A. H. GEISLER,† STUDENT ASSOCIATE, AND R. F. MEHL,* MEMBER A.I.M.E.

(New York Meeting, February 1941)

THE complicated nature of the property changes that accompany age-hardening has made it necessary to reconsider and to elaborate the simple dispersion theory.¹ It has been apparent for some time that more direct information is needed concerning the atomic mechanism of precipitation from solid solution if the theory of age-hardening is to be developed past a purely qualitative stage.‡ Fortunately, in recent years information has been developed which allows us to trace in detail the lattice changes accompanying the process of precipitation from solid solution. This information relates chiefly to the sequence of the several stages of lattice alteration by which the matrix lattice is transformed to the equilibrium precipitate lattice, and permits reasonable inferences to be drawn concerning the states of internal strain that accompany these stages.

This information is most complete for the solid solution of copper in aluminum. The equilibrium precipitate is the θ phase, "CuAl₂." This forms in plates, parallel to the {100} matrix planes. The atom pattern and atom spacing on the plane in θ lying parallel to this plane are roughly similar to those opposite it in the matrix.³ The formation of θ , however, is preceded

by the formation of a transition lattice θ' , which again lies parallel to the matrix {100} plane, but in this case the matching of atom pattern and spacing across the matrix-precipitate interface is nearly perfect; thus there is lattice coherency across the interface and the interface is a plane of separation in only a very limited sense.⁴⁻⁸ Particles of θ' may be recognized microscopically and form a well-defined Widmanstätten figure.*

The θ' lattice is recognized by the occurrence of diffraction lines on powder photographs or of spots on Laue photographs which may be analyzed in the usual ways to determine the lattice type and the lattice spacings. Very recent research^{6,7,1} has shown, however, that streaks occur on the Laue photograph at an earlier point in time during the aging process. These streaks have been attributed to a preferential clustering of copper atoms into small platelike elements of only a few atoms in thickness and a few hundred atoms in diameter, probably of the composition of "CuAl₂," which may be designated as Guinier-Preston zones or aggregates.¹ It is difficult if not impossible to determine the lattice type and lattice spacing in these aggregates. It is possible¹ that these aggregates are in fact merely θ' in a high state of dispersion; the inclination to argue this is strong, as we shall see later. Never-

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¹ References are at the end of the paper.

‡ Studies of the crystallography of Widmanstätten figures have had this as their chief aim.²

* It was foreseen by Merica that restraints to lattice movements imposed by lattice registry would lead to the formation of transition lattices.⁹

theless, in the interests of conservatism, these aggregates will be designated as a separate stage in the process of precipitation.

These aggregates in the aluminum-copper system are again parallel to the {100} matrix planes. It appears that the hardening is associated with either the Guinier-Preston aggregate or θ' or both,⁴⁻⁸ and that this hardening originates in the high degree of strain between these and the matrix. The equilibrium lattice θ , however, contributes relatively little to hardness, for in this case accurate registry across the interface does not obtain; the precipitate particle has broken away from the matrix with the release of strain. When this occurs in the aluminum-copper system, the θ particle (formed only at high temperatures on long-time aging) is already too large to be considered as contributory to hardening on the basis of the original age-hardening theory. It is to be noted that recent studies have thrown some doubt upon the conception of a critical dispersion of precipitate for maximum hardening,¹⁰⁻¹² and that accordingly this point may not be significant. Approximate values of the stress necessary to maintain lattice registry across the interface have been calculated.

The sequence of stages in precipitation in this system is accordingly as follows: matrix, Guinier-Preston aggregates, θ' , and finally θ . The precipitation reaction is thus in fact a series of consecutive reactions. These stages are related, however, not only in a genetic sense—that the transition lattice is formed from the Guinier-Preston aggregate, and the equilibrium lattice from the transition lattice, but also in a geometrical sense, for each is in the form of plates parallel to the same matrix plane and has an orientation closely allied to that of the preceding stages. This similarity in geometry suggests strongly that the three stages represent only different stages in a process of alteration in lattice geometry, the several stages differ-

ing only in the degree of completion of this alteration.^{1*}

This argument is based on one example only. It might well be argued that the occurrence of a common conjugate or interface plane throughout the three consecutive stages may be fortuitous and should not be used as the basis of a general theory. If, however, a system could be chosen that forms a platelike Widmanstätten figure on some matrix plane other than the {100}, and if it could be shown that the Guinier-Preston aggregate (and perhaps a transition lattice also) forms on this same plane, it could be more urgently argued that the Guinier-Preston aggregate is but an early stage in the development of the final equilibrium lattice, in which the lattice movements that ultimately will convert the matrix lattice to the equilibrium lattice have already begun.

An opportunity to test this argument is offered by the precipitation of the γ phase from the solid solution of silver in aluminum. Studies of the Widmanstätten figure in this system² have shown that the close-packed hexagonal intermediate solid solution γ forms plates parallel to the {111} plane in the matrix. On the basis of the argument, we may predict, therefore, that the Guinier-Preston aggregate and a transition lattice, if formed at all, will be plate-shaped elements lying parallel to this same plane.

The present paper will present evidence for the correctness of this prediction. The alloy forms the Guinier-Preston aggregate, consisting of plates of which the orientation and approximate sizes have been determined; a transition lattice occurs, the structure and the orientation of which have been solved; from these data the

* In this view it is as justified to designate the formation of the Guinier-Preston aggregate as precipitation as it is so to designate the formation of either of the latter two stages.¹ Although this is a debatable point, we shall use the word "precipitation" in this sense in the present paper.

lattice shifts necessary to transform the matrix lattice through the several stages to the equilibrium lattice have been derived; the nature and the approximate magnitude of the stresses associated with the formation of the transition lattice, and the release of these stresses on the formation of the equilibrium lattice, have been studied.

THE SYSTEM ALUMINUM-SILVER

Silver dissolves in solid solution in aluminum up to 48 weight per cent at the eutectic temperature 558°C. This solid solubility decreases to nearly zero at 200°C. The alloy with 20 weight per cent Ag used in this study crosses the solvus curve on cooling at just under 450°C. The solid solution of silver in aluminum, hereinafter designated as δ , is in equilibrium below the eutectic temperature with the γ phase. The γ phase is an intermediate solid solution containing 85 to 90 weight per cent Ag. The composition of γ in equilibrium with δ does not vary with temperature.¹³

The δ phase is face-centered cubic and is a substitutional solid solution. Owing to the near identity of the atomic radii of aluminum and silver, the side of the unit cube does not vary with concentration, retaining the value for aluminum, 4.041 Å. The γ phase is close-packed hexagonal, with the atoms distributed at random, and with $a_0 = 2.879$, $c_0 = 4.573$, and $c_0/a_0 = 1.588$, when saturated with aluminum (85 weight per cent Ag).¹³

Well-defined Widmanstätten figures are formed on the decomposition of the δ phase.² It has been shown that these take the form of plates parallel to the $\{111\}$ δ planes. The orientation relationship is $\{111\}\delta \parallel \{00.1\}\gamma$, and $[1\bar{1}0] \parallel [2\bar{1}.0]$. Thus the basal planes of the hexagon in γ lies parallel to the octahedral plane in δ ; the pattern of atoms in each is hexagonal. These hexagons are simply superimposed at the interface with the close-packed directions parallel.²

Until recently it has been assumed that the precipitate on aging is the γ phase. Recently the occurrence of a transition lattice has been shown, though its structure has not been determined.¹⁴ This lattice we shall designate the γ' lattice. It appears that the hardening on aging is associated with the formation of this lattice and not the γ lattice.¹⁴

Preparation of Samples

An alloy of 20.2 weight per cent Ag was prepared by melting 99.97 per cent Al with 99.99+ per cent Ag in a graphite crucible under a potassium chloride flux, chill-casting and rolling to a reduction of about 85 per cent with intermediate anneals. The alloy was annealed 48 hr. at 550°C. for homogenization. From this stock, wires were drawn with reduction from 0.25 to 0.035-in diameter with two intermediate anneals to serve as samples for microscopic studies and for X-ray powder-diffraction studies. From the same stock large grains for Laue samples were grown in $\frac{1}{2}$ -in. square rods, by a strain-anneal method; individual crystals were cut out with a jeweler's saw, and carefully thinned by rubbing on emery paper and by deep etching, which in addition to thinning served also to remove strained metal. The aging treatments employed are listed below.

Powder Photograms—Experimental

The wire specimens described above were given a solution heat-treatment of approximately 1 hr. at 500° to 530°C. in evacuated glass tubes, and then quenched in ice water, upon which the tubes broke. One set of powder specimens (those used for aging at 173°C.) was prepared by filing; the powder was soaked 20 min. in an evacuated tube at 506°C., and quenched in ice water. Both wire and powder specimens, protected by enclosure in evacuated glass tubes, were placed in an aluminum block in a resistance furnace

controlled to $\pm 1^\circ\text{C}$., or immersed in a salt bath controlled to $\pm \frac{1}{2}^\circ\text{C}$. for aging treatments.

Powder photographs were made in a

be seen by comparing observed and calculated intensities (the latter uncorrected for the factors varying slowly with Θ). It is therefore concluded that γ' , which during

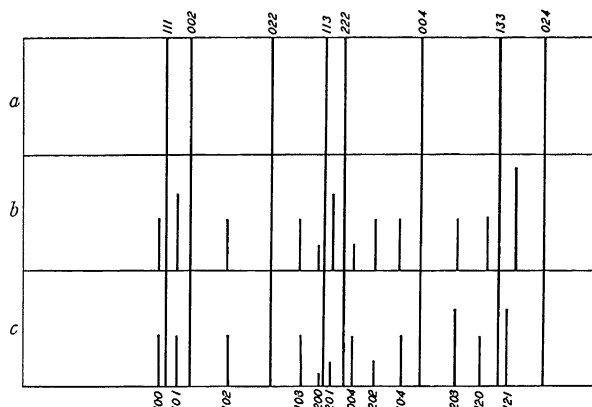


FIG. 1.—POWDER PHOTOGRAPHS OF ALLOY OF 20.2 PER CENT SILVER IN ALUMINUM.
a, spectrum of δ solid solution. As quenched from solution heat-treatment.
b, spectra of $\delta + \gamma'$. Quenched and aged 5 minutes at 387°C .
c, spectra of $\delta + \gamma$. Solution heat-treatment followed by cold-work; aged 16 hours at 175°C .

small cylindrical camera 2 in. in diameter and in some cases were duplicated in a $4\frac{1}{2}$ -in. camera. Direct radiation from a cobalt target operating at 37,000 volts was used. The specimens were rotated during exposure, which averaged one hour.

Results

The powder photographs showed that in addition to the equilibrium phase γ there is a transition lattice γ' .¹⁴ Typical diffraction spectra are listed in Fig. 1. In Fig. 1*a* the diffraction lines of the δ solid solution are alone present; in Fig. 1*b* the transition lattice γ' lines appear in addition to the δ lines; and in Fig. 1*c* the γ lines appear in addition to the δ lines. The $K\alpha$ lines from the γ' structure that did not overlap lines of δ or γ are listed in Table 1; it will be seen that their $\sin^2 \Theta$ values are fully accounted for by the quadratic form for the hexagonal system. The intensities are adequately accounted for by assuming a random distribution of atoms upon a close-packed hexagonal structure lattice, as will

precipitation precedes the γ phase, is a hexagonal close-packed solid solution (dis-

TABLE 1.—Powder-diffraction Lines from γ' Lattice

| Indices | Intensity | | $\sin^2 \Theta$ | |
|---------|-----------|------------|-----------------|------------|
| | Observed | Calculated | Observed | Calculated |
| 10.0 | M | 4 | 0.131 | 0.1302 |
| 10.1 | S | 18 | 0.166 | 0.1678 |
| 10.2 | M | 6 | 0.280 | 0.2805 |
| 10.3 | M | 18 | 0.469 | 0.4684 |
| 20.0 | W | 3 | 0.520 | 0.5207 |
| 20.1 | S | 18 | 0.559 | 0.5505 |
| 00.4 | W | 4 | 0.599 | 0.6014 |
| 20.2 | M | 6 | 0.673 | 0.6711 |
| 10.4 | M | 6 | 0.733 | 0.7316 |
| 20.3 | M | 18 | 0.859 | 0.8590 |
| 12.0 | M | 6 | 0.911 | 0.9113 |
| 12.1 | VS | 36 | 0.949 | 0.9489 |

$$\sin^2 \Theta = 0.13018 (h^2 + hk + k^2) + 0.03759l^2$$

$$\text{CoK}\alpha = 1.7866 \quad a_0 = 2.858 \quad c_0 = 4.607$$

$$\frac{c_0}{a_0} = 1.612$$

ordered) with $a_0 = 2.858$, $c_0 = 4.607$, and $c_0/a_0 = 1.612$. The similarities between this lattice and the matrix on one hand and the equilibrium lattice γ on the other hand provide an insight into the atomic

movements during aging. These movements are simple and may be stated in detail with considerable assurance of their reality, as we shall see below.

also contains streaks that must be distinguished from the aging streaks. The streaks in Fig. 2*h*, from pure aluminum, are caused by thermal agitation of the

TABLE 2.—*Aging of Annealed Wires and Structures Present after Aging*

| Aging Temperature, Deg. C. | | | | | | | | | | | | | | |
|----------------------------|-------------|---------------|--------------------|--------------------|--------------------|--------------------|----------------------|----------------------|--------------------|--------------------|--------------------|-----------------------|-----------|--|
| 160.... | Time, hr. | 1 | 4 | 12 | 24 | 48 | 96 | | | | | | | |
| | Precipitate | | | | | | γ' | | | | | | | |
| 173.... | Time, hr. | 1 | 21 | 47 | 72 | 120 | 192 | | | | | | | |
| | Precipitate | | | γ' | γ' | γ' | γ' | | | | | | | |
| 228.... | Time, hr. | $\frac{1}{2}$ | $1\frac{1}{2}$ | 2 | 6 | 12 | $18\frac{1}{2}$ | 27 | 48 | 96 | 120 | 168 | 240 | |
| | Precipitate | | γ' | γ' | γ' | γ' | γ' | γ' | γ' | γ' | γ' | $\gamma' + \gamma(?)$ | γ' | |
| 302.... | Time, hr. | $\frac{1}{2}$ | $\frac{1}{4}$ | $\frac{1}{2}$ | $1\frac{1}{6}$ | 3 | 12 | 24 | 48 | 96 | 120 | | | |
| | Precipitate | | γ' | γ' | γ' | γ' | γ' | $\gamma' + \gamma$ | $\gamma' + \gamma$ | $\gamma' + \gamma$ | $\gamma' + \gamma$ | | | |
| 387.... | Time, hr. | $\frac{1}{2}$ | $\frac{1}{2}$ | $1\frac{1}{2}$ | | 5 | 9 | 25 $\frac{1}{2}$ | 48 | 120 | | | | |
| | Precipitate | | γ' | γ' | | $\gamma' + \gamma$ | $\gamma' + \gamma$ | $\gamma' + \gamma^a$ | γ | γ | | | | |
| 440.... | Time, hr. | $\frac{1}{2}$ | $\frac{1}{2}$ | 1 | 2 | 5 | 10 | 16 $\frac{1}{2}$ | | | | | | |
| | Precipitate | γ' | $\gamma' + \gamma$ | $\gamma' + \gamma$ | $\gamma' + \gamma$ | $\gamma' + \gamma$ | $\gamma' + \gamma^a$ | $\gamma' + \gamma$ | | | | | | |

^a γ' and γ in about equal amounts.

The sequence of the appearance of γ' and γ was determined by the aging treatments listed in Table 2. All aging treatments from 160° to 440°C. first brought out the spectrum of γ' and later γ , the latter increasing in intensity at the expense of γ' and indicating that γ is formed by a transformation of γ' into the stable phase γ . This behavior is similar to that shown by the θ' and θ phases in aluminum-copper alloys.⁴⁻⁸

Laue Photographs

The size, shape, and orientation of the precipitating particles in the early stages of aging are conveniently shown by Laue photographs. These were made with the radiation from a cobalt target at 37,000 volts, with exposures varying from 2 to 12 hr. The analysis of the streaks and spots in the Laue patterns has been presented in detail in a previous paper¹⁵ and will be mentioned only briefly here. Typical patterns are reproduced in Figs. 2*a* to 2*h*. In all Laue photographs shown here, the X-ray beam penetrated the crystal along [001] with [100] vertical; other orientations were analyzed but need not be reproduced. It is necessary first to show the pattern for pure aluminum, since it

atoms¹⁶⁻¹⁸ and are always radial. The streaks from the aluminum-silver alloy during aging are not radial, but follow ellipses (see, for example, Figs. 2*a* and 2*d*). By plotting the streaks on a stereographic projection, in the way Laue spots are commonly plotted, it has been found that the streaks correspond accurately to great circles passing through the four {111} poles, and from a consideration of the reciprocal lattice or the Fourier transform, it is clear that this means that the lattice regions giving rise to the streaks have a relaxed third Laue condition; i.e., these regions are thin plates, responding to X-rays approximately as crossed gratings, and that these regions are therefore Guinier-Preston aggregates, lying upon the {111} matrix planes. Similar diffraction effects have been observed in aluminum-copper alloys,^{6,7} as mentioned above, but there is an important crystallographic difference between the two cases: in aluminum-silver alloys the thin plates are on the {111} planes, whereas in aluminum-copper the gratings are on {100} planes.

From the diffuseness of the streaks and the intensity distribution along them, the approximate thickness and diameter of the Guinier-Preston aggregates can be

estimated, using the formulas for line widening from the particle size effect. The dimensions corresponding to the patterns in Fig. 2 are listed in Table 3 in the order

TABLE 3.—*Approximate Dimensions in Å. of Precipitate Corresponding to the Laue Patterns of Fig. 2*
LISTED IN ORDER OF INCREASING SIZE

| Fig. | Thickness | Diameter |
|------|-----------|----------|
| 2b | <10 | <100 |
| 2c | <10 | <100 |
| 2a | <10 | <100 |
| 2d | <10 | >100 |
| 2e | 10 to 100 | >100 |
| 2f | 10 to 100 | >100 |
| 2g | >100 | >100 |

of increasing size. At some stages of aging it is clear that there is a considerable range of particle size, but Table 3 lists only the larger ones. In Fig. 2c the streaks are so diffuse as to be invisible except where they overlap with other streaks. In this state the Guinier-Preston aggregate has a diameter of less than 100Å. and a thickness of a very few atom layers. Aging

manstätten structure in this system.² By this time the precipitate has grown to a thickness sufficient to afford three-dimensional diffraction, and the particles are 10^{-6} cm. or more in all dimensions. Figs. 2e and 2f are somewhat earlier stages in the growth, where the thickness is roughly 10 to 100Å. All of the Laue patterns obtained can be classified among the types illustrated in these figures. A summary of the aging treatments given one of the crystals studied is provided in Table 4, with the corresponding classification of the pattern after each treatment. The crystal was first given a solution heat-treatment of 16 hr. at 556°C., then quenched into a mixture of dry ice and acetone. Fig. 2a was obtained from the specimen in this state, indicating that the quench had not entirely suppressed the formation of precipitate. After the 20° aging experiments listed in the table, the crystal was rehomogenized for 15 hr. at 530°C., and quenched in ice water, and aged at 150°C.; subsequent aging treatments followed a similar sched-

TABLE 4.—*Aging Treatments Yielding Types of Patterns of Fig. 2 and Interpretation in Table 3*

| Aging Temperature, Deg. C. | | | | | | | | | | | | |
|----------------------------|-----------------|----|----|----|----|-----|-----|----|----|----|----|----|
| 20..... | Time, days | 0 | 7 | 22 | 50 | 150 | 280 | | | | | |
| | Type of pattern | 2a | 2a | 2c | 2c | 2c | 2c | | | | | |
| 150..... | Time, hr. | 0 | 1½ | 2 | 11 | 26 | 32 | 40 | 47 | 59 | 66 | 82 |
| | Type of pattern | 2a | 2b | 2c | 2c | 2c | 2c | 2c | 2c | 2c | 2c | 2d |
| 200..... | Time, hr. | 0 | 1½ | ¼ | ¾ | 1½ | 2½ | 3 | | | | |
| | Type of pattern | 2a | 2b | 2b | 2b | 2b | 2e | 2f | | | | |
| 320..... | Time, hr. | 0 | 1½ | | | | | | | | | |
| | Type of pattern | 2a | 2g | | | | | | | | | |
| 400..... | Time, hr. | 0 | 1 | | | | | | | | | |
| | Type of pattern | 2a | 2g | | | | | | | | | |

produces streaks of progressively increasing sharpness, and when the patterns of type 2d are obtained, there is no longer any appreciable widening arising from a limited diameter of the precipitate. When the aging is continued for about 1 hr. at 320°C., or for shorter times at higher temperatures, new spots begin to appear along the Laue streaks (as in Fig. 2g) at positions demanded by the orientation relationships derived in an earlier study of the Wid-

ule. Air-cooling the specimen produced the type of pattern shown in Fig. 2f. Experiments with other crystals will not be reported in detail, for they were less complete and afforded no additional information except showing that the various stages are passed through at different rates in different crystals.

The times in Table 4 are not accurately comparable with the times in Table 2, for the latter were derived from data on poly-

crystalline wires. A further limitation to the time scales in the tables is that the appearance of the X-ray films is somewhat dependent on the amount of exposure

very thin plates of γ' . Whatever the arrangement of atoms in the cluster, the fact that it forms on the (111) is good evidence that the lattice movements that

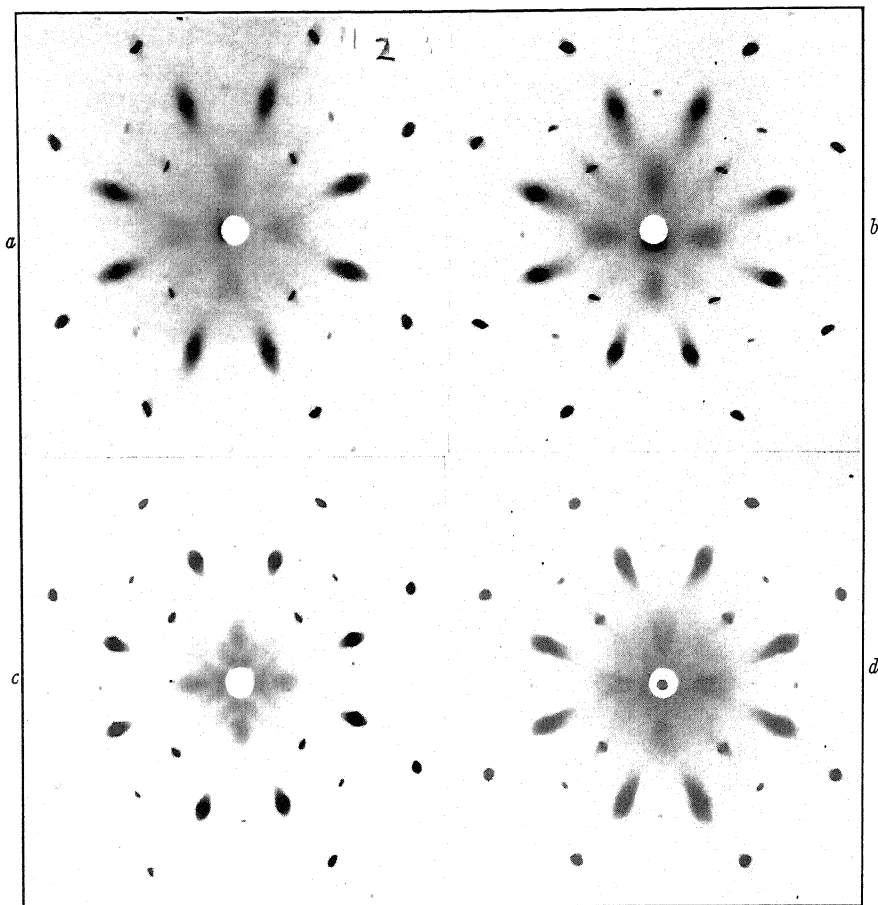


FIG. 2.—LAUE PHOTOGRAMS OF A SINGLE-CRYSTAL

- a*, as quenched from solution heat-treatment.
b, aged 5 minutes at 200°C.
c, aged 50 days at room temperature.
d, aged 104 hours at 150°C.

given: Type 2c can be made to look like 2b by underexposure.

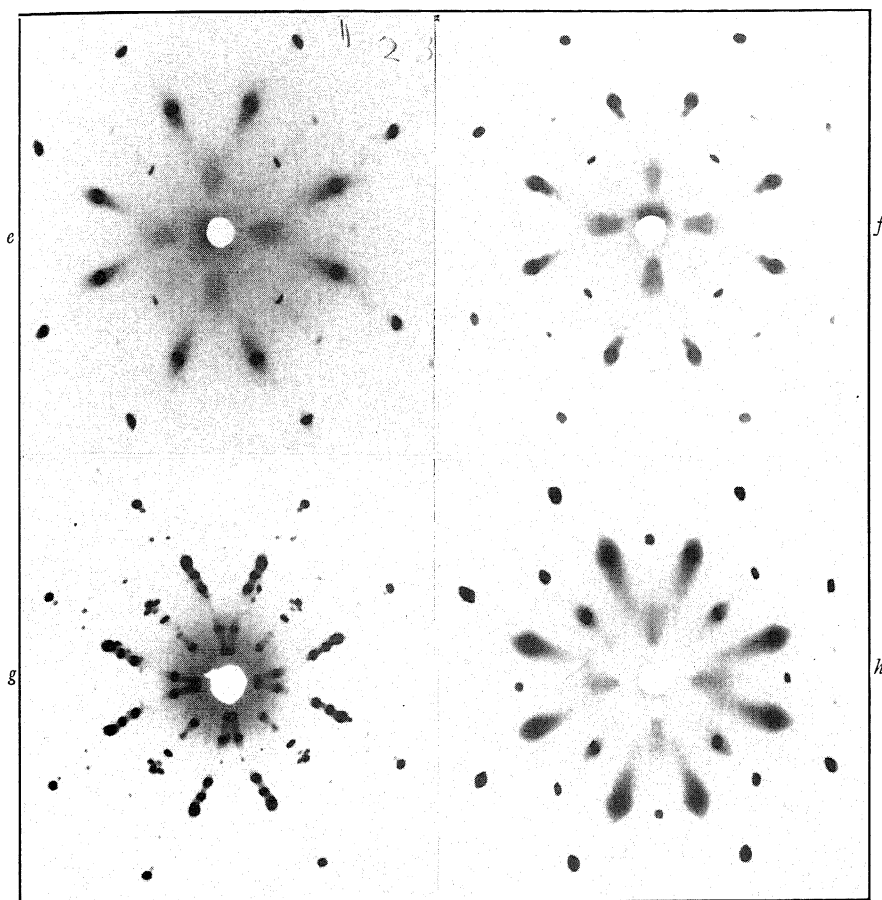
Despite the uncertainties in comparing the single-crystal and polycrystalline experiments, it can be definitely stated that the origin of the streaks in the Laue photographs is not the equilibrium phase γ , but is either platelike clusters of silver atoms on the (111) planes of the matrix, or simply

ultimately form γ have already begun. In the lack of evidence to the contrary, we strongly incline to the view that the clusters are in fact very small particles of the transition lattice γ' .*

* A similar suggestion has been made above with respect to the similar set of circumstances in the aluminum-copper system.

It happens that the axial ratios of γ' and γ differ so little that they cannot be distinguished on Laue photograms; but the sequence of changes given in Table 4

shows that the γ' phase alone forms a well-developed Widmanstätten figure (no γ has yet formed in this specimen); a count of the number of different trace directions in



X-RAY BEAM ALONG $[001]$ WITH $[100]$ VERTICAL.

e, aged $2\frac{1}{2}$ hours at 200°C .

f, aged 3 hours at 200°C .

g, aged 1 hour at 320°C .

h, 99.97 per cent aluminum annealed 11 hours at 500°C and quenched.

clearly indicates that the sharp spots, when they first appear in the Laue photograms, are γ' instead of γ .

Microstructure

Photomicrographs of some of the polycrystalline wires used for the X-ray photograms are reproduced in Figs. 3, 4, and 5. Fig. 3, of a specimen aged 5 min. at 387°C .,

each of several grains confirms the expectation that the plates of γ' are on (111) planes of the matrix. Another specimen aged for 30 min. at the same temperature exhibits unusually long markings; apparently a number of parallel plates have grown laterally until they extend entirely across grains of the matrix. The precipitate is again wholly γ' . Fig. 5, of a specimen aged

25½ hr. at the same temperature, shows plates again in a Widmanstätten pattern. X-rays show that this specimen contains γ' and γ in approximately equal amounts. Direction counts of a number of these grains again confirm (111) precipitation.*

Samples containing γ' were difficult to etch; the microstructures observed (Figs. 3 and 4) are somewhat diffuse and the edges of the γ' plate not clearly resolved. This was observed even when the γ' plates are relatively large. Plates of γ , however, were readily resolved, possessing well-defined sharp edges. Gayler¹⁹ made similar observations on aluminum-copper alloys; she experienced difficulty in developing a sharp edge along one of the sides of rectangular θ' plates, and took this as separate evidence of a coherency between θ' and the matrix. Such evidence, resting upon minor variations in etching attack and in arrangement and orientation of very small particles, is rather uncertain.

Orientation Relationships

It has been mentioned above that the first nuclei to give diffraction effects, the Guinier-Preston aggregates, are thin plates lying parallel to (111) planes of the matrix. It is shown by the Laue streaks that close-packed rows of atoms in the plane of these nuclei are parallel to the close-packed rows in the (111) matrix planes against which they lie.†

At a later stage, when the γ' particles

* From the approximate rates of the reaction γ' to γ established in the present study, it follows that the earlier Widmanstätten paper was concerned largely with the equilibrium phase, though some of the specimens may have contained both γ' and γ , but since the two lattices are indistinguishable in habit and only slightly different in structure, the crystallographic statements of the earlier paper need no amendment.

† This is most readily seen in diagrams of the reciprocal lattice¹⁵ from the fact that each streak of the Laue photographs corresponds in reciprocal space to a line passing through the corresponding points of the reciprocal lattice of the matrix. The development of precipitate spots reproduced in Figs. 2e, 2f, and 2g, together with the analysis of 2g¹⁵ also confirm this.

have grown large enough to diffract as three-dimensional gratings, the same orientation relationship holds, as can be deduced from the position of the diffuse precipitate spots in Figs. 2e and 2f¹⁵ and the sharp precipitate spots in Fig. 2g. A further proof is provided by the portion of a powder-diffraction pattern enlarged and reproduced in Fig. 6. In this, two rows of spots are shown close to each other, with each intense spot of the stronger row matched by an identical spot just opposite it in the weaker row. The stronger row consists of (111) spots from the matrix; the weaker row consists of (0001) spots from the precipitate, which is known to be γ' by its full spectrum on the same film. The photogram was prepared by rotating the polycrystalline wire and therefore is a rotating crystal pattern of a number of differently oriented grains; from the geometry of such patterns it can be shown that only with the orientation relationships as stated above could there be the one-to-one correspondence between the two rows of spots seen in Fig. 6. A similar pairing of spots also appears in the second-order lines from these same planes.

When γ' decomposes to γ , there is no reason to expect an alteration of orientation, for the former can be regarded as the latter under elastic strain, as we shall show later. The orientation is retained in rotating polycrystalline wire photographs similar to Fig. 6, which show (111) and (0001) spots opposite each other (in both first and second orders). More direct proof is afforded by Laue photographs of single crystals that have been aged at high temperatures until there could be no question but that all the precipitate is γ . These give patterns indistinguishable from Fig. 2g, proving the orientation mentioned (see reference to Fig. 2g above).

Discussion of Results

There can be no doubt that there is complete registry between the basal plane of γ' and the (111) plane of the matrix on which it forms, for the atomic array on

these two planes is identical in pattern, interatomic distances, and orientation. Interatomic spacings that do not lie in this plane are altered, however; the (111) plane

of planes of the face-centered lattice, $ABCABC \dots$, is altered into the sequence for the hexagonal close-packed lattice, $ABABAB \dots$. These movements

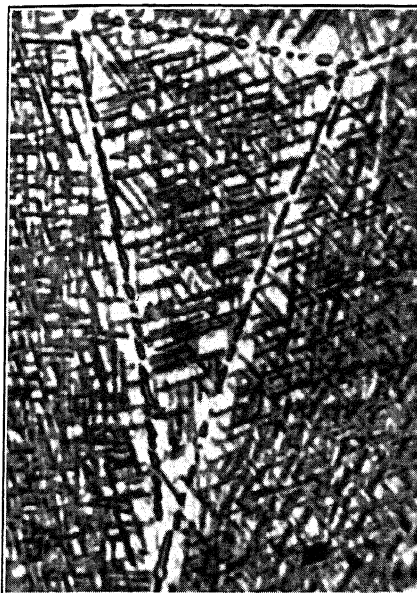


FIG. 3.—POLYCRYSTALLINE WIRE AGED 5 MINUTES AT 387°C. $\times 2500$. PRECIPITATE IS γ' .



FIG. 4.—POLYCRYSTALLINE WIRE AGED 30 MINUTES AT 387°C. $\times 2500$. PRECIPITATE IS γ' .

Etched in 0.5 per cent HF.

spacing of δ , $d_{(111)}$, contracts 1.4 per cent in forming the (0001) planes of γ' . On forming γ from γ' there is a further contraction of 0.74 per cent in the (0001) plane spacing, $d_{(0001)}$, and an expansion of 0.73 per cent in all atomic distances lying in this plane. These facts provide a basis for a consistent theory of the sequence of lattice changes.

At those regions in the matrix where statistical fluctuations have produced a sufficiently high silver content,* parallel (111) planes of the matrix move over one another during precipitation in such a way as to convert the face-centered cubic lattice into the hexagonal close-packed lattice. This movement is in the direction $[10\bar{1}0]$. If shifts of this kind take place with proper regularity, the sequence

are illustrated in Fig. 7. Fig. 7a shows the face-centered cubic δ lattice with (111) as the base plane; in forming the γ' lattice, shown in Fig. 7b, the upper two atom layers of the four shown move to the left, in the direction indicated by the arrows, taking positions at the tips of the arrows; the extent of translation is the same for these two layers. This produces the γ' lattice shown in Fig. 7b, as comparison of these two figures will show. The horizontal atom spacing does not change in the formation of γ' , but the perpendicular spacing decreases somewhat (1.4 per cent). In the formation of γ , shown in Fig. 7c, there is no translation of atom layers, but merely a readjustment of all atom spacings.*

* This crystallographic mechanism is identical with that proposed earlier for the same alloy² except that the earlier description did not include a consideration of the intermediate γ' step, which was then unknown; the mechanism

* See discussion of concentration fluctuations given in ref. 1.

It has been suggested¹⁵ that the shifting of (111) layers of atoms necessary to create γ' might have occurred in an irregular fashion to yield the Laue streaks observed.



FIG. 5.—POLYCRYSTALLINE WIRE AGED 25½ HOURS AT 387°C. X 2000. PRECIPITATE IS $\gamma' + \gamma$.

Etched in 0.5 per cent HF.

For example, the plane sequence of the matrix $ABCABC \dots$ may change to the sequence of $\gamma' ABABAB \dots$ through an intermediate stage of staggered irregular sequence, e.g. $ABABCABABABC \dots$. But such a lattice would in fact be merely matrix + γ' in a lamellar arrangement. The postulated shifting can thus create only γ' from the matrix—there appears to be no possibility of the formation of an intermediate lattice between

proposed introduced the idea of shearing movements into considerations of phase changes of this type.

the matrix and γ' . This reasoning supports the assumption that the Guinier-Preston aggregate is only γ' in a fine state of subdivision.

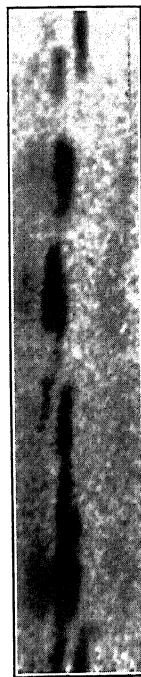


FIG. 6.—ENLARGED PORTION OF POWDER PATTERN CONTAINING $\delta + \gamma'$ SPECTRA.

Spots on (111) δ ring paired with weaker spots on (0001) γ' showing parallelism of these planes. Specimen aged 1½ hours at 387°C.

It is obvious that the matrix δ must strive to form the γ immediately. The shearing movements of atom layers, which is the major lattice alteration necessary for the conversion of δ to γ , operates immediately, but the atoms on the (111) matrix plane cohere to the atoms opposite on the (0001) γ' , preventing a change in their spacing until during growth the strain which this entails becomes intolerable. At the γ' stage, therefore, the precipitate lattice has not broken away from the matrix, but strains the matrix and is itself strained by the matrix. The contraction of 1.4 per cent normal to the (0001) plane can probably be accom-

modated by the matrix lattice without the formation of a crack at the interface, because of the thin platelike shape of the precipitate.¹⁰⁻¹² With increasing thickness

Fig. 2c, were observed after aging at and below 150°C. but not after aging above this temperature. These streaks are characteristic of an extremely small particle

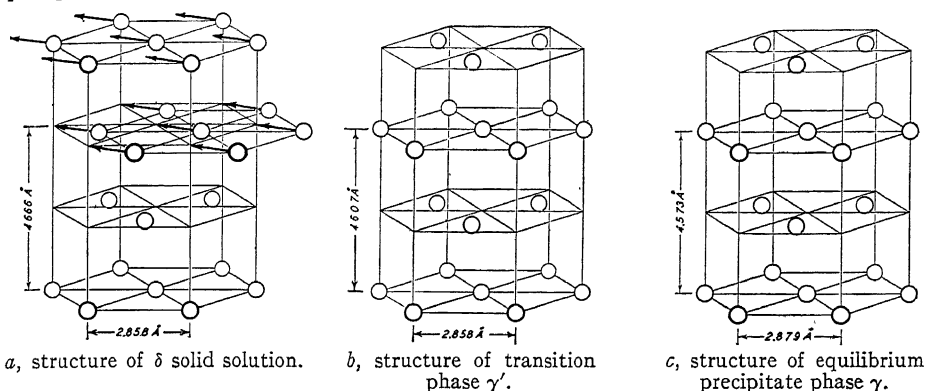


FIG. 7.—CRYSTAL LATTICE OF PHASES PRESENT IN AGED ALLOYS.

of the γ' plates and the consequent increasing strain, the tendency to break away increases and finally prevails, permitting the precipitate to take the lattice dimensions of γ .

From the appearance of the high order diffraction lines of γ , it may be concluded that the transition from γ' to γ is a sudden one without intermediate steps; when the disregistry once begins, the precipitate probably snaps all the way to its final dimensions.*

Nucleation theory requires that the smallest stable nuclei of the precipitate increase in size with increasing aging temperature. There is support for this proposed variation of nuclei size with aging temperature in the evidence presented in Fig. 2 and Table 4. The most diffuse streaks, those which give the patterns of

size. The streaks obtained by aging above 150°C. are sharper and are therefore evidence of larger particles of γ' . The quenching, though extremely severe, was unable to suppress all nucleation, for patterns like Fig. 2a were always obtained from the quenched alloy. It is interesting that in most of the experiments of Table 4 the streaks of Fig. 2a were observed to first become much weaker, as in Fig. 2b before the intense sharp streaks of the later stages of aging appeared. This suggests that the particles present after quenching may have redissolved in part before a new set was precipitated.

If γ' is merely γ held by elastic strains from assuming the normal lattice spacings of γ , it seems justified to calculate the magnitude of the stresses in γ' from the known values of the strains. The elastic constants of the γ phase are unknown, but a rough idea of the magnitude of the stresses can be obtained by assuming the elastic constants for either aluminum or silver (which do not differ greatly) and applying the elastic theory equations for an isotropic medium. Let the stresses be referred to two orthogonal axes, X and Y , in the basal plane and a third, Z , along

* The transition from γ' to γ is not unlike slip, for it involves displacements on slip planes. From this similarity, it seems reasonable to expect an instantaneous jump from γ' to γ when the stresses at the interface, aided by thermal agitation, start the displacement, for when any point on the interface breaks out of registry, there is a situation similar to that postulated in the recent theories of slip, in which slip resistance is thought to be greatly reduced by disregistry ("dislocation") on the slip plane.

the c axis of the crystal; the three principal stresses σ_x , σ_y , σ_z are related to the three principal strains ϵ_x , ϵ_y , ϵ_z by the three simultaneous equations

$$\begin{aligned}\epsilon_x &= [\sigma_x - \nu(\sigma_y + \sigma_z)]/E \\ \epsilon_y &= [\sigma_y - \nu(\sigma_x + \sigma_z)]/E \\ \epsilon_z &= [\sigma_z - \nu(\sigma_x + \sigma_y)]/E\end{aligned}$$

Now ϵ_x , ϵ_y and ϵ_z may be evaluated from the difference between the lattice dimensions of γ' (strained) and γ (unstrained) in the X , Y , and Z directions and have the following values: $\epsilon_x = \epsilon_y = (2.858 - 2.879)/2.879 = -0.0073$; $\epsilon_z = (4.607 - 4.573)/4.573 = 0.0074$. Inserting these values in the equations and assuming the values of $E = 10,300,000$, $\nu = 0.34$ as in aluminum alloys (the corresponding values for silver would not alter the calculations significantly) the following stresses are obtained in pounds per square inch:

$$\begin{aligned}\sigma_x &= \sigma_y = -115,000 \\ \sigma_z &= -1,800\end{aligned}$$

where the negative sign indicates compression. The value $-1,800$ for σ_z is, of course, less than the error of measurement and calculation and could as well be considered zero, permitting the assumption that all stresses exerted by the matrix on the precipitate are directed parallel to the basal plane—as if the precipitate is glued to the matrix (111) plane—and that there are negligible stresses normal to this plane (the c -axis contraction resulting from the basal plane stresses only). It might be pointed out that the matrix is unable to exert great stresses in the direction of the c axis of the precipitate, because of the platelike shape of the particles,¹⁰⁻¹² which may explain the low value. It is also conceivable that there is an actual crack along one face of the precipitated plate, where the plate has been drawn away from the matrix by the contraction resulting from the formation of γ' , but this is unlikely. The contraction is so slight that it would

amount to as much as half of the interplanar spacing $d_{(111)}$ only if the plates were about 100\AA . thick or more; that is, in a late stage of the process. The strain in the matrix around the edges of the γ' plates seems appropriate to facilitate further growth of the plate edgewise, for it must be contracted toward the spacing $d_{(0001)}$ of γ' , and may account for the extended plates of Fig. 4.

The sequence of events discussed above are in entire accord with the expectations outlined in earlier papers¹ and with Nabarro's theoretical treatment of stresses.¹⁰⁻¹² Assuming that the breaking away of a precipitated particle from the matrix plane on which it forms requires roughly the same energy as the melting of a monatomic layer of metal at the surface of the particle, Nabarro calculates that the particle will break away when its thickness equals

$$c_{11}\Delta J\rho/(c_{11} + 2c_{12})(c_{11} - c_{12})\delta^2$$

where c_{11} and c_{12} are the elastic moduli, Δ the latent heat of melting, J is the mechanical equivalent of heat, and δ is the misfit between the two lattices in the matched plane. If the constants for silver are inserted, the thickness for breaking away is roughly $107 \times 10^{-4}/\delta^2$ and for the case that Nabarro considered, the precipitation of silver from copper, breaking away will occur when the particle is only two atoms thick. But in the present instance, where the misfit between the unstrained (111) and (0001) planes is only $(2.879 - 2.858)/2.858 = 0.0073$, the same constants would predict breaking away at about 320 atom layers, or 730\AA . The theory is thus in accord with the fact that sharp Debye rings can be obtained from γ' before it becomes large enough to break away and become γ .

The stresses in the matrix that keep the precipitate in the strained γ' condition are beyond much doubt an important contributor to the hardening.²⁰ It is an old

idea that strains are set up during aging and that these are important in producing age-hardening. The theories were based on the volume changes accompanying precipitation and more vaguely on precipitate matrix interaction, but in recent years^{1,4-8,20} the importance of the effect of registry on strain has been pointed out. In the aluminum-silver system considered here, there is a decrease in volume on the formation of γ from the δ solid solution, from 16.50 to 16.47 Å.³ per atom; thus broken-away γ does not fit perfectly into its space in the δ lattice and strain must result, but this must exert a minor hardening effect, for it is observed that the formation of γ from γ' in the aluminum-silver system and of θ from θ' in the aluminum-copper system are accompanied by softening. Evidently at least in these systems a different origin of strain must be sought.

With the demonstration of orientation relationships between precipitate and matrix,² and with the correlated near-matching of atom patterns and spacings at the interface and the strains implied by this imperfect registry, a basis is available for a more detailed study of age-hardening strains. When transition lattices occur, as they do in the aluminum-copper and aluminum-silver systems, the state of strain is more clearly apparent and the degree of strain is susceptible to calculation. Such strains obviously must interfere with slip and thus harden; they may also be at least in part responsible for the "anomalies" occurring in property changes during age-hardening.¹ Further progress in the theory of age-hardening will be facilitated by a more detailed understanding of the intensity and distribution of these strains in the matrix. It appears possible to make approximate calculations of these in the present instance with elastic theory formulas and this is being attempted.

The Guinier-Preston aggregate, the transition lattice, and the equilibrium

precipitate lattice in the aluminum-silver system are similarly arranged geometrically. In the aluminum-copper system the same geometrical similarity obtains among the same stages, but the geometrical arrangement itself differs from that for aluminum-silver alloys. In each case the geometry of the Widmanstätten figure formed by the equilibrium precipitate appears also in the earlier stages. It appears therefore that the several lattice stages accompanying precipitation from solid solution may be regarded simply as successive steps in a single process of lattice alteration, which converts the matrix lattice to the lattice of the equilibrium phase.

SUMMARY

1. The lattice changes that accompany precipitation from the solid solution of silver in aluminum (20 per cent Ag) have been studied.

2. This alloy forms Guinier-Preston aggregates, platelike in shape, upon the (111) matrix plane. These aggregates are small at low aging temperatures and larger at high aging temperatures; they grow with aging times. Their approximate sizes have been determined. It is possible that the aggregates are merely the transition lattice γ' in a high degree of dispersion.

3. The alloy forms a transition lattice, γ' , that is close-packed hexagonal. It also is platelike in shape and deposited on the (111) matrix plane. The spacing in γ' on the (0001) γ plane is identical with the atom spacing on the (111) matrix plane to which it lies parallel; the lattices are therefore coherent at this interface. Since the γ' lattice differs from the equilibrium precipitate lattice γ only in interatomic distance, γ' may be regarded as γ strained from its ordinary dimensions by the lattice coherency between it and the matrix. The magnitude of this strain has been calculated, and the stresses that cause it have been computed.

4. The lattice movements that transform the matrix to the equilibrium precipitate lattice have been inferred from the orientation relationships observed.

5. Since the Guinier-Preston aggregate, the transition lattice γ' and the equilibrium lattice are all arranged in a similar way geometrically, it may be concluded that these stages in precipitation are merely successive steps in a single process of lattice alteration, which converts the matrix lattice to the lattice of the equilibrium phase.

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DISCUSSION

(W. L. Fink presiding)

D. W. SMITH,* New Kensington, Pa.—I wish to congratulate the authors on this very excellent paper. Dr. Barrett, in particular, deserves our appreciation for his lucid explanation of Guinier-Preston zones given in the oral presentation.

The authors point out two possible mechanisms of precipitation: (1) a three-stage process in which Guinier-Preston zones are formed in some distinct but unknown manner, then actual precipitation of a second phase having a transition lattice structure, and finally a transformation of the precipitate to the equilibrium lattice structure; and (2) a two-stage process, which makes no distinction between the formation of Guinier-Preston zones and the precipitation of a transition phase but which recognizes the transformation of the precipitate to the equilibrium structure.

Let us examine the facts to establish which of the two mechanisms appears the more logical. In the first place, the X-ray method used to detect the formation of the so-called Guinier-Preston zones is not capable of distinguishing between an agglomeration of solute atoms on certain crystallographic planes of the solvent lattice in the form of thin platelets (which was that condition originally proposed by Guinier and Preston) and the actual precipitation of a second (transition lattice) phase in the same form. Furthermore, the present authors have shown a distinct difference in location of the Guinier-Preston zones depending on the alloy system—in Al-Cu

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alloys the zones form parallel to the {001} planes of the aluminum-solid solution while in Al-Ag alloys they form parallel to the {111} planes of the aluminum-solid solution. Finally, Dr. Mehl and his collaborators have already shown, in their studies on Widmanstätten structures, that the precipitate phases form as plates parallel to the same planes to which the Guinier-Preston zones lie parallel in the respective parent solid solutions.

In view of these facts, it seems logical that the two-stage precipitation mechanism should be given more emphasis than the three-stage process, because: If the Guinier-Preston zones were merely local regions of high concentration of either copper or silver atoms in the parent solid solution, it would be expected that their location would be controlled only by the lattice type of the parent solid solution; on the other hand, if they were small precipitate platelets, they would be expected to form according to some orientation relationship (Widmanstätten) between the parent and precipitate lattices, which is the true case.

L. W. KEMPF,* Cleveland, Ohio.—Speculation regarding the proper nomenclature for the Guinier-Preston phenomena is interesting and useful. It appears that the term *precipitation* by general consent and usage will be utilized in referring to all the events accompanying the disintegration of supersaturated solid solutions in spite of the much more limited meaning assigned to the term by the general theory of heterogeneous equilibria.

Perhaps an even more interesting field for speculation is the correlation between structure and mechanical properties. Nothing appears in the paper regarding hardness or other mechanical properties. On the basis of data gathered some time ago on alloys of this type, I would expect maximum hardness to be reached with not more than about 20 hr. aging at 150°C. or not more than 2 or 3 hr. at 200°C. As is usual in such precipitation-hardening systems, the hardness will probably be higher the lower the aging temperature. If approximately these relationships hold for the alloy investigated by the authors, it would appear that maximum hardness and presumably maximum strength are achieved prior to the appearance of appreciable quantities of γ' or γ . In other words, in

this system, and perhaps also in the aluminum-copper system, the formation of Guinier-Preston zones is the most effective hardening process; and the development of appreciable quantities of γ' and γ from these zones results in softening. I wonder whether the authors have any data that might be used to establish a correlation between the structure and properties of the alloy they investigated?

C. S. BARRETT AND R. F. MEHL (authors' reply).—Dr. Smith is clearly in agreement with the final paragraphs of the Discussion of Results and the Summary but believes that more emphasis should be given to the theory that the Guinier-Preston aggregate is merely γ' in a fine state of dispersion. This theory was the keynote of the paper, it will be noted, and the authors went as far as they thought was justified when the paper was written. The experimental work has been continued on these and other alloys and it is now possible to report additional support for the theory.

During precipitation from aluminum-rich alloys of aluminum and magnesium, it is possible to observe streaks on Laue photograms that are very similar to those in aluminum-copper alloys. Analysis of these and of the Widmanstätten structure shows that the streaks are caused by thin plates forming on the (100) planes of the aluminum-rich matrix. The important factor in this experiment is the very close similarity in scattering power between the aluminum and magnesium atoms. The two kinds of atoms are so nearly alike in their ability to scatter X-rays that it would be impossible to detect mere segregation of magnesium atoms on the lattice of aluminum with the type of photogram we have used. Accordingly, we must ascribe the Laue streaks in this system to small platelike regions in which the structure is no longer than that of the matrix and has become that of the transition lattice, or perhaps has become an irregular structure that may be described as a mixture of the two or a compromise between the two. We have suggested and discussed an irregular or incomplete transition lattice in the paper of reference 15. This is the first case that has been investigated in which the segregation theory and the precipitation theory can be directly distinguished experimentally, and the fact that Laue streaks are found is more direct

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support for the precipitation theory than has been given by any of the previous observations. The reasoning advanced in the paper and reviewed by Dr. Smith leads to the conclusion that in other alloy systems also there is no distinction between the formation of what we have called Guinier-Preston aggregates and true precipitation.

We agree with Dr. Kempf that the term "precipitation" may well be applied to all events accompanying the disintegration of the solid solution. Hardness measurements have now been made and correlated with powder diffraction spectra of γ' and γ in the aluminum-silver system and it is definitely established

that the transition lattice γ' alone can be seen in alloys aged to their maximum hardness. For example, with a 20 per cent silver alloy the maximum hardness with aging at 225°C. is reached in about 3 hr.; γ' first appears in the powder patterns in one hour, whereas the stable precipitate γ does not appear until the alloy is very much overaged (more than 40 days in one experiment). Similar results have been obtained with 10 and 30 per cent Ag alloys. It is safe to conclude that the hardening is not related to the stable phase in this system, but probably is associated with the stresses surrounding the particles of the transition lattice as has been pointed out in the paper.

Precision X-ray Study of the High-silver Aluminum-silver Alloys

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(Cleveland Meeting, October 1940)

IN recent years the constitution of the high-silver aluminum-silver alloys has been extensively investigated. Hansen¹ has reviewed the literature to 1935. More recently, Obinata and Hagiya,² Hofmann and Volk,³ Taziri⁴ and Tishchenko⁵ have confirmed the general features of the phase diagram in the region around 25 atomic per cent aluminum.

In this paper we present the results of high-precision measurements of lattice constants of the silver-rich alpha solid solution in the homogeneous range and the neighboring two-phase regions. These results are used to establish the nature of the solid solution, the identity of directly measured densities with those calculated from lattice constants and the homogeneity limits of the alpha solid solution with respect to three different neighboring phases. A study of the earlier investigations indicated that the last two subjects in particular required new and accurate data.

EXPERIMENTAL PROCEDURE

Preparation of the Alloys.—The alloys were made from high-purity silver and aluminum. The silver was "Proof Silver," 99.999 per cent pure, supplied by the U. S. Metals Refining Co. The aluminum was 99.97 per cent pure (contained Si, 0.009 per cent; Fe, 0.0016 per cent; Cu, 0.004 per

cent) and was supplied by the Aluminum Company of America. The lattice constants of these two materials have been reported by Jette and Foote.⁶ Weighed amounts of the two metals were placed in alundum crucibles and melted in vacuo in a high-frequency induction furnace. The melts were allowed to cool in the crucible, the ingots thus obtained weighed about 10 grams. These ingots were then filed clean, hamered, again cleaned and given a homogenizing anneal in vacuo of from 6 to 15 days at temperatures ranging from 500° to 695°C. The ingots were air-cooled from the annealing temperature.

Lattice-constant Measurements.—Carefully prepared filings for X-ray analysis were sealed into evacuated quartz or Pyrex tubes and annealed for various periods of time at suitable temperatures. The furnaces used were vertical, rapid-quenching furnaces, the samples being quenched by crushing the sample tube under water by means of a heavy plunger.

The general X-ray technique has been previously described.⁶ The cameras were of the symmetrical, back-reflection, focussing type. K_{α} radiation from a cobalt-nickel alloy target was used. The wave-length values were taken from the second edition of Siegbaum's book.⁷ A correction for the index of refraction was applied and the lattice constants were calculated by the method of Cohen.^{8,6} The lattice constants were calculated to a common temperature of 25°C., using the value of the linear expansion coefficient of pure silver as 18.9×10^{-6} . Presumably the expansion coefficient for

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¹ References are at the end of the paper.

the high-silver solid solution is not far different from that of pure silver and in any case the correction is very small.

Density Measurements.—The density of three of the single-phase alloys was determined by the loss-of-weight method. The density liquid was mono-brom-benzene. The density of the brombenzene was calculated from the equation given in International Critical Tables (vol. 3, p. 29). This equation was checked by pycnometer weighings and found to be essentially correct. As a density liquid, brombenzene has a number of advantages. It is easily purified by simple distillation, has a high density of about 1.5 grams per cubic centimeter, moderate viscosity, low vapor pressure and low surface tension. The samples used were annealed filings. All measurements were corrected to 25°C. using $3 \times 18.9 \times 10^{-6}$ for the volume coefficient of expansion. In all cases, this correction was small.

Chemical Analysis.—All alloys were analyzed for aluminum by precipitating as $\text{Al}(\text{OH})_3$ with ammonium hydroxide and weighing as Al_2O_3 , closely following the method given by Hillebrand and Lundell.⁹ The method was checked by analyzing synthetic mixtures containing known amounts of silver and aluminum. The analytical values were close to the values calculated from the weights of the pure metals used in making the alloys. Determinations were made on annealed filings used for the density and X-ray measurements and on millings from the annealed ingots. No significant differences between these values were found. All compositions were converted to atomic per cent, using for the atomic weights: Ag, 107.88; Al, 26.97.

Lattice Constants and Densities of the Single-phase Alloys.—The lattice-constant data for the single-phase alloys have been tabulated in Table I and plotted in Fig. 1. The heat-treatments refer to the final powder anneal. The standard errors of the the lattice-constant measurements average 0.00010 A_{gr} . The data can be satisfactorily

represented by the least-squares straight line:

$$a_0 = 4.07787 - 0.001253 (\text{At \% Al}) \quad [1]$$

The average deviation of the individual measurements from this line is 0.00010 A_{gr} .

TABLE I.—*One-phase Alloys*

| Alloy | Heat-treatment | | Atomic Per Cent Al | Lattice Constant, a_0 (25°C.) |
|-------|----------------|----------|--------------------------|---------------------------------------|
| | Hr. | Deg. C. | | |
| Ag | (Ave. of 7) | (ref. 6) | 0.00 | 4.07787 |
| 1 | 2 | 721 | 4.00 | 4.07288 |
| 12 | 116 | 548 | 10.76 | 4.06452 |
| 2 | 2 | 721 | 11.22 | 4.06382 |
| 11 | 146 | 538 | 14.24 | 4.05980 |
| 4 | 2 | 693 | 15.75 | 4.05794 |
| 4 | 40 | 500 | 15.75 | 4.05793 |
| 3 | 2 | 721 | 17.35 | 4.05626 |
| 3 | 40 | 500 | 17.35 | 4.05608 |
| 3 | 1.5 | 720 | 17.35 | 4.05592 |
| 7 | 112 | 598 | 17.45 | 4.05621 |
| 7 | 5 | 520 | 17.45 | 4.05589 |
| 10 | 116 | 548 | 18.28 | 4.05522 |
| 10 | 230 | 598 | 18.28 | 4.05518 |

Equation 1 can be solved for atomic per cent Al:

$$\text{At \% Al} = 3255.16 - 798.250(a_0) \quad [2]$$

The average deviation of the individual measurements from this line is 0.08 atomic per cent Al. The lattice constants show large negative deviations from Vegard's rule.

Westgren and Bradley,¹⁰ Ageew and Shoyket,¹¹ Barrett¹² and Phelps and Davey¹³ have previously measured the lattice constants of certain of these high-silver alloys. The results of the first three of these investigations were somewhat higher than those reported in this paper; the results of the fourth were considerably lower. Westgren and Bradley measured the lattice constants of two alloys within the solid solution range; their claimed precision was 0.002 A_{gr} . Hume-Rothery pointed out in discussion¹¹ that the results of Ageew and Shoyket were neither self-consistent nor properly handled. Barrett's results showed the quenching effect¹⁴ obtained with samples of moderate

size. The results of Phelps and Davey are entirely out of line with other determinations and cannot be considered as precision measurements.

in which n is the number of atoms per unit cell, M is the average atomic weight, a_0 is the lattice constant in "crystal Ångströms" (i.e., $10^3 \times$ units), N is Avogadro's number

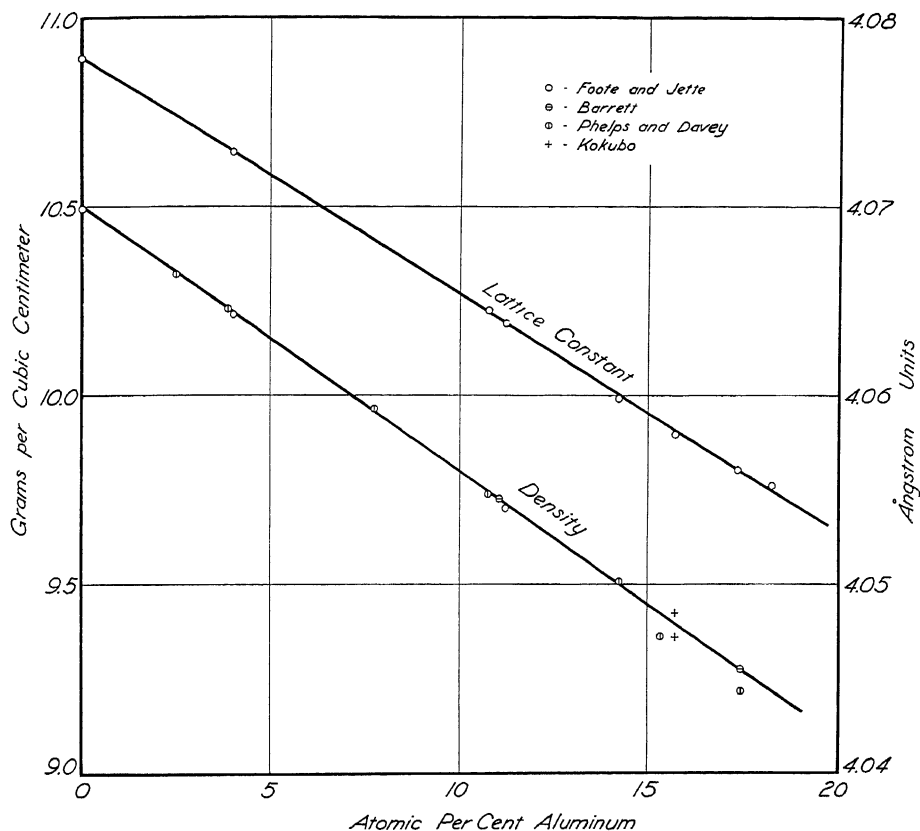


FIG. 1.—LATTICE CONSTANTS AND DENSITIES OF SINGLE-PHASE ALLOYS.

Phelps and Davey,¹³ Barrett,¹² Kokubo¹⁵ and the present authors have measured the densities of a number of these high-silver solid solution alloys. The data are summarized in Table 2 and plotted in Fig. 1. With a few exceptions, the measured densities agree very well among themselves. The solid line of Fig. 1 is the theoretical density calculated on the basis of simple substitution of aluminum for silver atoms in the silver lattice. The formula used for this calculation was:

$$\rho = \frac{10^{24} n M}{f^3 N a_0^3} \quad [3]$$

and f is the ratio between the absolute and the relative Siegbaum scale of X-ray wave lengths. Jette and Foote¹⁶ have evaluated the factor $K = 10^{24}/f^3 N$ from published data on calcite. The numerical value of K was found to be 1.65023 ± 0.00021 . The density formula thus becomes:

$$\rho = 1.65023 \times \frac{nM}{a_0^3} \quad [3']$$

where: $n = 4$

$$M = 107.88 - 0.8091 (\text{at. \% Al})$$

(simple substitution)

$$a_0 = 4.07787 - 0.001253 (\text{at. \% Al})$$

(eq. 1)

The last column of Table 2 gives the comparison between the measured and calculated densities. For the most part, the agreement is excellent. In particular, the agreement with Barrett's measured densi-

TABLE 2.—*Density of Single-phase Alloys*

| Ob-server ^a | Atomic Per Cent Al | Lattice Constant a_0 (25°C.), Calculated | ρ (25°C.) | | $\Delta\rho \times 10^3$ |
|------------------------|--------------------|--|----------------|--------------------|--------------------------|
| | | | Calcu-lated | Meas-ured | |
| FJ | 0.00 | 4.07787 | 10.501 | 10.492 | -9 |
| B | 0.00 | 4.07787 | 10.501 | 10.489 | -12 |
| PD | 0.00 | 4.07787 | 10.501 | 10.50 | -1 |
| PD | 2.47 | 4.07477 | 10.330 | 10.32 | -10 |
| PD | 3.85 | 4.07304 | 10.234 | 10.23 | -4 |
| FJ | 4.00 | 4.07286 | 10.224 | 10.213 | -11 |
| PD | 7.76 | 4.06814 | 9.961 | 9.966 | +5 |
| PD | 10.81 | 4.06432 | 9.747 | 9.737 | -10 |
| B | 11.04 | 4.06404 | 9.731 | 9.726 | -5 |
| B | 11.04 | 4.06404 | 9.731 | 9.727 | -4 |
| FJ | 11.22 | 4.06381 | 9.718 | 9.701 | -17 |
| PD | 14.25 | 4.06001 | 9.503 | 9.507 | +4 |
| PD | 15.36 | 4.05862 | 9.424 | 9.362 | -62 |
| K | 15.75 | 4.05814 | 9.397 | 9.423 ^b | +26 |
| K | 15.75 | 4.05814 | 9.397 | 9.361 ^c | -36 |
| B | 17.48 | 4.05597 | 9.273 | 9.274 | +1 |
| B | 17.51 | 4.05593 | 9.271 | 9.273 | +2 |
| PD | 17.51 | 4.05593 | 9.271 | 9.216 | -55 |

^a FJ, Foote and Jette; PD, Phelps and Davey; B, Barrett, K. Kokubo.

^b Cast, cold-worked and annealed.

^c Cast and annealed.

ties is uniformly good and considerably better than the agreement with his own calculated densities. We may conclude that there is no significant difference between directly measured densities and those calculated from X-ray data, provided both sets of measurements are carefully done and the proper formula used for the density calculation. This fact has not previously been fully established. Furthermore, in view of the close agreement between the measured and calculated densities, we are justified in believing that the solid solution of aluminum in silver is of the simple substitutional type¹² and that any other, more complex, theory of solid solution is unnecessary.¹³

Solid Solution Limit.—Data on the two-phase alloys used in determining the alpha homogeneity limits are tabulated in Table 3 and plotted in Fig. 2. The solid solubility limit was calculated by substituting the

measured values of the lattice constants in eq. 2. Also, in Fig. 2, the liquidus as determined by Hoar and Rowntree¹⁷ and the solidus as determined by Hume-Rothery, Mabbott and Evans¹⁸ are plotted.

In order to keep the alpha-phase lines strong and to avoid interference by the lines of the second phase (particularly by the gamma phase), it is desirable that the two-phase alloys be only slightly higher in aluminum than the homogeneity limit. At the same time, we must be sure that the alloys are actually two-phase. In doubtful cases, the samples were photographed in an identification camera (Phragmén type) to check the presence or absence of the second phase.

TABLE 3.—*Two-phase Alloys*

| Alloy ^a | Heat-treatment | | Lattice Constant, a_0 (25°C.) | Solubility Limit |
|--------------------|----------------|---------|---------------------------------|------------------|
| | Hr. | Deg. C. | | |
| 5 | 1 0 | 748 | 4.0548 ₅ | 18.37 |
| 5 | 0 5 | 737 | 4.0549 ₀ | 18.26 |
| 5 | 2 5 | 698 | 4.0542 ₆ | 18.84 |
| 5 | 3 | 693 | 4.0542 ₆ | 18.84 |
| 13 | 6 | 655 | 4.0533 ₇ | 19.55 |
| 14 | 6 | 655 | 4.0534 ₀ | 19.53 |
| 14 | 43 | 617 | 4.0525 ₀ | 20.25 |
| 14 | 40 | 602 | 4.0523 ₈ | 20.34 |
| 14 | 329 | 574 | 4.0524 ₈ | 20.26 |
| 14 | 341 | 507 | 4.0528 ₂ | 19.99 |
| 14 | 490 | 453 | 4.0527 ₅ | 20.05 |
| 13 | 490 | 453 | 4.0530 ₂ | 19.83 |
| 5 | 747 | 430 | 4.0540 ₀ | 18.57 |
| 5 | 5 | 412 | 4.0557 ₃ | 17.67 |
| 10 | 407 | 401 | 4.0564 ₅ | 17.10 |
| 10 | 744 | 374 | 4.0581 ₅ | 15.74 |
| 10 | 453 | 352 | 4.0599 ₄ | 14.31 |
| 11 | 1173 | 306 | 4.0615 ₀ | 13.06 |
| 11 | 5491 | 263 | 4.0638 ₉ | 11.16 |
| 11 | 1124 | 198 | 4.0671 ₅ | 8.56 |

^a Total compositions:

| ALLOY | ATOMIC PER CENT AL |
|-------|--------------------|
| 5 | 20.5 |
| 13 | 20.0 |
| 14 | 21.5 |
| 10 | 18.3 |
| 11 | 14.2 |

The solid solubility limit is not a continuous line, but consists of three distinct parts. The breaks at B and C correspond to changes in character of the second phase. The portion AB represents the solubility limit with beta, BC with gamma, and CD with beta prime (Ag₃Al) as the adjoining phase.

The point *A* (obtained by extrapolation to 779°C., the peritectic temperature found by Hoar and Rowntree) is placed at 17.84 atomic per cent Al. The break in the solu-

mines the temperature at which the peritectoid reaction for the formation of Ag_3Al takes place. Point *C* is placed at 452°C. and 19.92 atomic per cent Al. This tem-

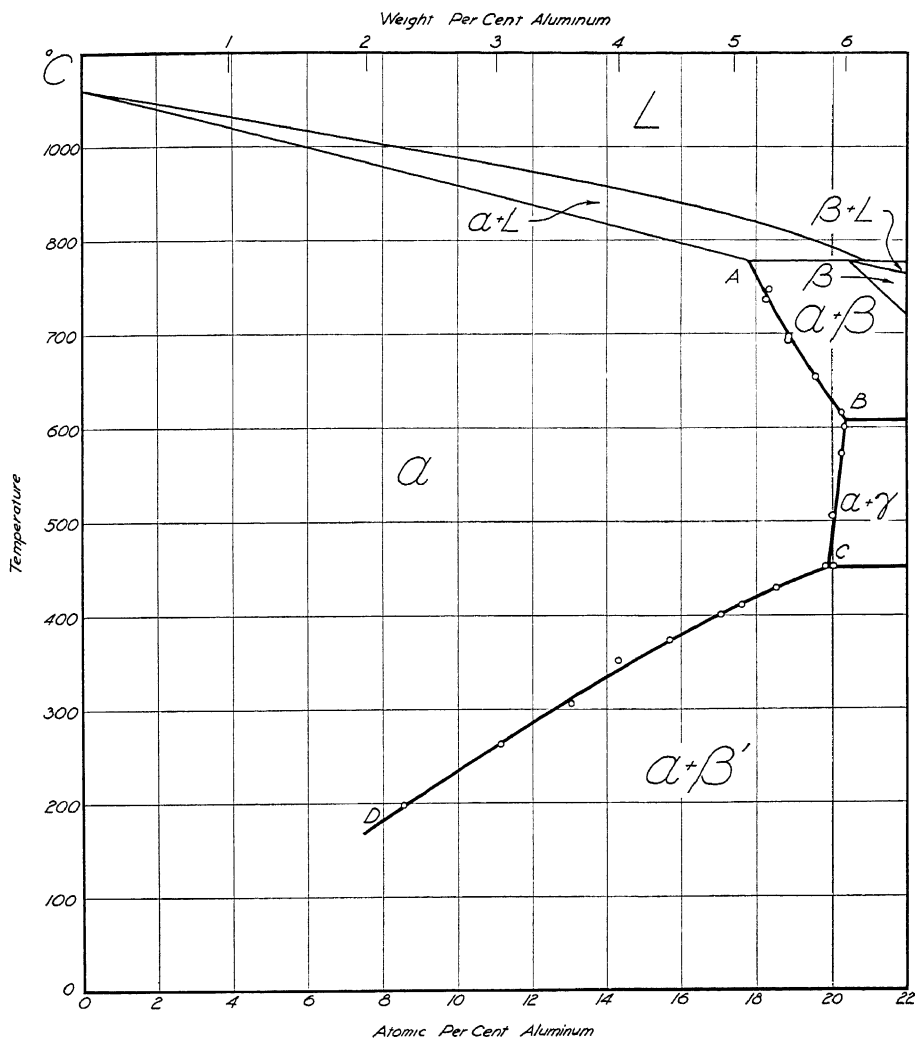


FIG. 2.—PHASE DIAGRAM OF HIGH-SILVER ALUMINUM-SILVER ALLOYS.

bility limit at *B* determines the eutectoid temperature for the decomposition of the beta phase. This point is placed at 609°C. and 20.34 atomic per cent Al. The eutectoid temperature has been previously reported at 615°C.,² 610°C.,^{11,19} 609°C.,²⁰ 606°C.,^{5,21} and 570° to 605°C.³ The break at *C* deter-

perature has been previously reported as 456°C.,⁵ 420°C.,² 400°C.,¹¹ and 370° to 465°C.³ It is of considerable interest that the eutectoid and peritectoid temperatures can be accurately determined by careful X-ray determinations on the solid solution limit.

The portion *AB* of the solubility limit represents an interesting application of the X-ray method. As is well known, the beta phase cannot be retained, while the alpha phase can be retained by quenching. Consequently, films of two-phase alloys quenched from this temperature range show sharp lines from the alpha phase and blurred lines from the products of the beta decomposition. The X-ray method can be used therefore to determine accurately solubility limits of a quenchable phase, even though the phase with which it is in equilibrium cannot be retained by quenching. (Cf. Jette and Foote²² on Fe-Ni, and Mathewson²³ on Ag-Hg alloys quenched from the alpha plus liquid regions.) In this temperature range, the solubility of aluminum in silver increases somewhat with decreasing temperature.

The portion *BC* of the solubility curve represents equilibrium between the alpha and gamma phases, both of which can be retained by quenching. In this temperature range, the solubility of aluminum in silver decreases slightly with decreasing temperature.

Below the peritectoid temperature (i.e., with beta prime as the adjoining phase), the solubility of aluminum in silver decreases rapidly with decreasing temperature. The filings for the X-ray analysis were annealed for long periods of time in order to approach true equilibrium as closely as possible. In all cases, equilibrium was approached from the same side; i.e., by the precipitation of beta prime from the alpha phase. The fact that widely different annealing times gave solubility limits that yield a smooth curve when plotted against annealing temperature indicates that the heat-treatments were adequate. Another criterion of equilibrium is the sharpness of the X-ray lines. If the phases present are not of uniform composition, X-rays will be diffracted over a range of angles and the lines would be blurred. In all cases, sharp lines were obtained.

Hoar and Rowntree¹⁷ and Hume-Rothery, Mabbott and Evans¹⁸ have determined the solid solution limit by microscopic methods. Of a total of 29 microscopic observations by these investigators only 5 fall in the wrong phase fields, and even these are very close to the solid solution limit as determined by X-ray methods. Thus, if the X-ray and microscopic methods are carefully and properly applied, the results on solid solubility determinations are in complete agreement. In other words, the phase diagram is truly a function of the system itself and is independent of the method used to investigate the system. Cases of such complete agreement between these two methods of investigation are not common.

Ageew and Shoyket¹¹ have reported considerably higher solubility limits as a result of X-ray and microscopic studies. Their alloys were given short anneals and it is very doubtful whether equilibrium had been attained.

SUMMARY

Precision lattice-constant measurements have been made on silver-rich alpha solid solution alloys of the silver-aluminum sys-

TABLE 4.—*Summary of Solubility Limit*

| Temperature, Deg. C. | Atomic Per Cent Al | Weight Per Cent Al | Adjoining Phase |
|-------------------------|--------------------------|--------------------------|--------------------|
| 779 ^a | 17.84 | 4.67 | |
| 750 | 18.18 | 4.77 | Beta |
| 700 | 18.85 | 4.98 | Beta |
| 650 | 19.62 | 5.22 | Beta |
| 609 ^b | 20.34 | 5.44 | |
| 550 | 20.19 | 5.40 | Gamma |
| 500 | 20.06 | 5.35 | Gamma |
| 452 ^c | 19.92 | 5.31 | |
| 400 | 17.02 | 4.42 | Beta prime |
| 300 | 12.52 | 3.13 | Beta prime |
| 200 | 8.75 | 2.12 | Beta prime |

^a Peritectic temperature, $\alpha + L \rightleftharpoons \beta$

^b Eutectoid temperature, $\beta \rightleftharpoons \alpha + \gamma$

^c Peritectoid temperature, $\alpha + \gamma \rightleftharpoons \beta'$

tem. In the homogeneous field, the lattice constants are a linear function of the composition (in atomic per cent). Densities

have been calculated from these lattice constants on the assumption of simple substitution of aluminum for silver atoms in the silver lattice. These calculated densities check the directly measured densities within the experimental error of the density measurements. The solid solubility limit has been determined over the temperature range of 200° to 779°C. The limit thus established is in close agreement with microscopic results reported by other investigators. The results of determinations of the solid solubility limit are summarized in Table 4.

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X-ray Analysis of Hot-galvanized Heat-treated Coatings

BY F. R. MORRAL,* MEMBER A.I.M.E., AND E. P. MILLER†

(Cleveland Meeting, October 1940)

HOT-DIPPED heat-treated zinc coatings on sheet steel were examined with X-rays. The phases identified were compared with those listed in the modern literature of the zinc-iron system. The zeta (FeZn_{13}) phase is shown to correspond to the phase found by Schueler (1925) in heat-treated zinc coatings.

An investigation was undertaken to determine the phases present in hot-dipped

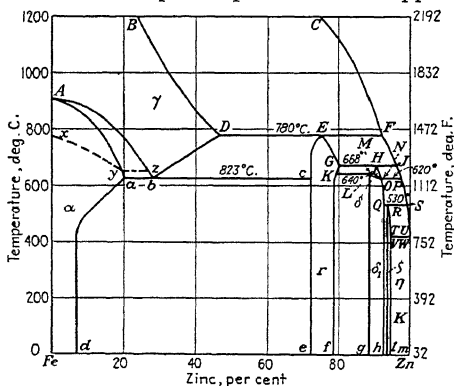


FIG. 1.—SYSTEM IRON-ZINC ACCORDING TO J. SCHRAMM.¹¹

heat-treated zinc coatings on steel sheets and wire. This kind of coating on wire was studied some years ago by Schueler¹ by microscopic and chemical methods. He reported a new phase, FeZn_{10} . Later, Clark and Stillwell,² using X-ray crystal analysis, identified a new phase in ordinary galvanized wire, which was assumed to be the FeZn_{10} phase.

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¹ References are at the end of the paper.

PREVIOUS WORK

Since the extensive review of the iron-zinc alloys presented a few years ago,³ much new work has been published, some of which⁵⁻¹⁶ was too late to be included in the recent edition (1939) of the American Society for Metals' Handbook.⁴

Figs. 1 and 2 are reproductions of the latest iron-zinc diagram proposed by

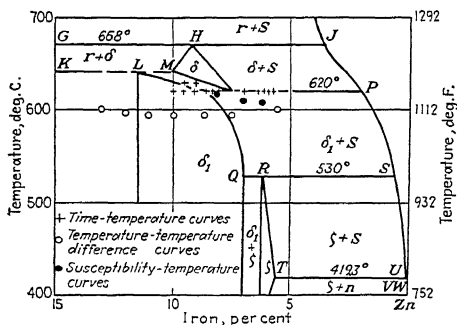


FIG. 2.—TRANSFORMATION OF δ IN δ_1 IN IRON AND ZINC SYSTEM.

Schramm¹¹ as a result of his investigations by microscopic, thermal, magnetic susceptibility and X-ray methods. Table 1 summarizes all the known published X-ray data of the phases present.

The solubility of iron in zinc has been determined by X-ray methods.¹⁰ In the same manner the homogeneity range of the Γ phase was studied¹⁰ using the principle that the parameter of an intermetallic compound changes while the concentration of one of the constituents changes.

Schramm¹⁰ has found some 80 alpha lines in X-ray powder photograms of phase δ_1 , and from these he believes that this phase is related to the Γ phase. Previous investi-

gators had considered this δ_1 phase to be hexagonal close packed¹⁷ with an axial ratio $c/a = 1.130$.¹² It is not a superstructure, but a gigantic cell containing 550 ± 8 atoms in the unit cell. This would make it the largest cell found to date among the intermetallic phases. More work seems to be desirable on the structure of the δ_1 phase.²⁴ The formula given is also uncer-

although having lower symmetry. Halla, Weil, and Goetzel's¹⁶ data for this phase are given in Table 1. They established definitely that FeZn_{13} is monoclinic. There are two molecules of FeZn_{13} per unit cell.

It has been mentioned before that a phase designated as FeZn_{10} was determined some time ago¹ by chemical analysis and

TABLE 1.—Phases in the Zinc-iron System

| Greek Letter | Phases | Formula, Per Cent Fe | | | Crystal Structure | Space Group | Atoms Elementary Cell | Parameter, Å. | Remarks |
|----------------|-------------|-------------------------------|--------------|---------------|-------------------|---|-----------------------|--|--|
| | | X-ray Data | Atomic | Wt. | | | | | |
| Alpha.. | α Fe | FeZn | | | b.c.c. | O_h^9 | 2 | 2.862–2.943 | Up to 400°C. dissolves 6 per cent Zn |
| Gamma | γ Fe | FeZn | | | f.c.c. | O_h^5 | 4 | Not determined | May dissolve as much as 43 per cent Zn |
| Capital Gamma. | Γ | $\text{Fe}_5\text{Zn}_{21}^a$ | 23 2 31 3 | 20 5 28 | b.c.c. | T_d^2 | 52 | 8.9560–8.9997 | ¹⁰ |
| | δ_1 | FeZn_7 (?) | 8.1 13.2 | 7– 11.5 | Hexagonal | $C_{6v}^4 = C_{6mc}$ or $D_{6h}^4 = C_{6hmc}$ | 550 ± 8 | $a - 12.80$ $c - 57.6$ $c/a - 1.1300$ ₁₂ | Present between room temp. and 640°C. ₁₀ |
| Delta.. | δ | FeZn_7 (?) | 8.1 11.5 | 7– 10 | | | | Not determined | 620–668°C. |
| Zeta... | ζ | FeZn_{13} | 7.2 7.4 | 6.0 6.2 | Monoclinic | $C_{2h}^3 - C_2/m$ | 28 | $a - 13.65$ $b - 7.61$ $\beta - 128^\circ 44'$ $c - 5.06$ | There are two molecules to the unit cell. ₁₈ |
| Eta.... | η | Zn | | Max. 0.003 | Hexagonal c.p. | D_{6h}^4 | 2 | $a - 2.6600$ $b - 4.9379$ $c/a - 1.8563$ | ^{4a} |

^a The Γ phase occasionally has been given the formulas FeZn_3 , $\text{Fe}_3\text{Zn}_{16}$,¹⁶ and $\text{Fe}_5\text{Zn}_{21}$.^{18,19} This last formula is to be preferred although it is not consistent with any regular distribution of the two kinds of metal ions between the points of the basic alpha-brass structure,²⁰ whose characteristic is the ratio of 21 electrons to 13 atoms. W. L. Bragg²¹ has stated that the relation between number of electrons and atoms in the structural unit overrides the influence of regular arrangement. Jones,²² using the reasoning of wave mechanics, has made a study of the energies of the loosely bound electrons in the alloys with the structure and found that the ratio of 21:13 comes very near to completely filling a zone. The magnetic properties are found to agree with such an arrangement. Thus, although the actual amounts of iron and zinc may not correspond to the relationship $\text{Fe}_5\text{Zn}_{21}$, it has the characteristic arrangement of atomic sites on which the conception of a phase is formed. In other words, Hume Rothery's rule²⁰ and Jones' theory,²² although indicating a definite number of atoms in the unit pattern, make no demand that the ratio of the atoms of different kinds should be represented by simple integers.²³

tain. No X-ray work has been done on the structure of the high-temperature delta phase.

Zeta,⁸ a new phase with a narrow range of homogeneity (6.0 to 6.2 per cent Fe by weight) has been established by thermal, microscopic, magnetic susceptibility and X-ray methods. The crystal structure was claimed¹⁰ to resemble that of the Γ phase,

found in large amounts in heat-treated zinc coatings. This phase was believed to correspond to the C phase found in galvanized wire coatings by X-ray diffraction.² A comparison of the Clark and Stillwell data for C phase (7 lines) with that of Schramm⁸ (52 lines) suggests the identity of this phase with $\text{Fe}_5\text{Zn}_{21}$. The first two investigators maintain that the new phase is body-

centered cubic, and the German author believes that it is cubic of low symmetry.

EXPERIMENTAL PROCEDURE

Samples from a commercial galvanized sheet taken at random were submitted to X-ray diffraction analysis. The sheet was hot-dipped in a "double-bottom" galvanizing pot^{25,26} and the coating was "gal-

solution of sulphuric acid to remove any superficial zinc oxide. After this treatment the weight of coating was 0.58 oz. per square foot of sheet. The analyses of the steel and of the coating are given in Table 2.

X-RAY DIFFRACTION ANALYSIS

The X-ray diffraction pictures were taken by allowing collimated unfiltered radiation

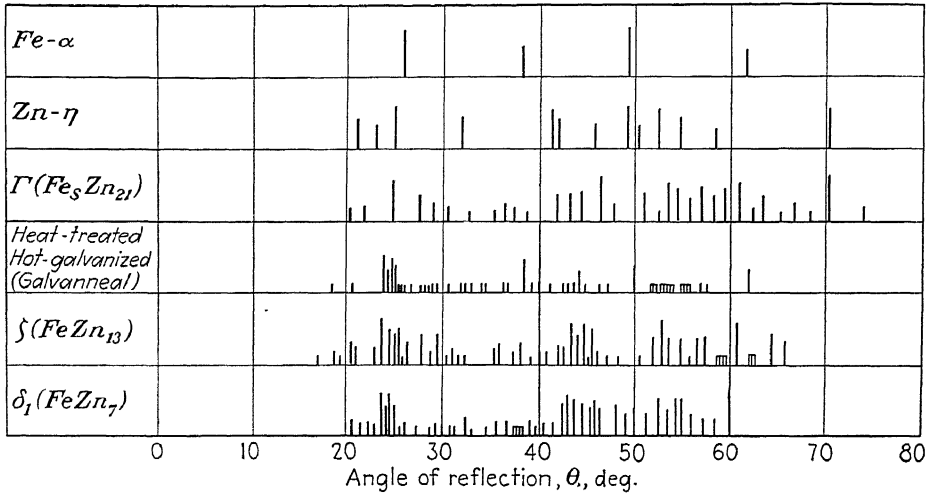


FIG. 3.—COMPARISON OF COMPOSITE X-RAY DIFFRACTION PATTERN OF HEAT-TREATED HOT-GALVANIZED COATING AND PATTERNS OF KNOWN IRON-ZINC ALLOYS.

vannealed,"^{1,27} a commercial process that consists in passing the freshly galvanized

TABLE 2.—Analyses of Steel and of Coating

| Sample | "Galvannealed" Sheet | Sample | "Galvannealed" Sheet |
|--------------------------------------|----------------------|---|----------------------|
| I. Analysis of base steel, per cent: | | II. Weight of coating, oz. per sq. ft. | |
| Carbon..... | 0.02 | 0.62 | |
| Manganese.... | 0.40 | III. Analysis of coating, per cent: | |
| Phosphorus.... | 0.085 | Iron..... | 10.02 |
| Sulphur..... | 0.057 | Lead..... | 1.07 |
| Silicon..... | Tr. | Tin..... | 0.34 |
| Copper..... | 0.30 | Zinc (by difference).... | 88.57 |
| Nickel..... | 0.26 | | |

sheet through a muffle furnace at 1200°F. for approximately 15 sec. when traveling at 60 ft. per minute. The sample was dipped for one minute in a 1.7 per cent by volume

to fall on the sheet sample at a glancing angle with its surface. The diffraction pattern was obtained on a film located on a cylindrical camera placed about the sample. The diameter of the camera used in this work was 15.229 centimeters.

The sample was examined at different glancing angles, to bring different regions of the picture into focus at different times. From these a composite table was made (Table 3). This composite picture was verified by making an X-ray diffraction analysis on heat-treated galvanized wire.*¹ The intensities of the lines were hard to evaluate on a composite diffraction photograph. They are indicated in Table 3 with

* The wire readings had to be corrected to take into consideration the fact that the diffraction occurs from several points on the surface.²

reservations. The angles indicated in the table refer to cobalt- $K\alpha_1$ radiation to permit comparison with published work.¹⁰

TABLE 3.—*Diffraction Pattern of Heat-treated Zinc Coatings*
ANGLES CALCULATED TO CO- $K\alpha_1$ RADIATION

| Fe- $K\alpha_1$ Radiation Intensity | Co- $K\alpha_1$ Radiation Angle | d_{hkl} , Å. | Source |
|---|---------------------------------------|-------------------|--|
| | 18° 20' | 2.84 | Zeta ($FeZn_{13}$) |
| | 20 36 | 2.53 | Zeta and Fe_3Zn_{21} |
| Strong..... | 23 57 | 2.197 | Zeta and Fe_3Zn_{21} |
| Medium..... | 24 23 | 2.161 | Zeta |
| Strong..... | 24 43 | 2.134 | $FeZn_7$ and Fe_3Zn_{21} |
| Weak..... | 25 | 2.112 | Zeta and Fe_3Zn_{21} |
| Medium..... | 25 17 | 2.09 | Zinc (2.08) |
| Very weak.... | 25 33 | 2.07 | Zeta |
| Weak..... | 26 9 | 2.025 | Zeta |
| Weak..... | 26 40 | 1.988 | Iron (110) 2.01 |
| Very, very weak..... | 27 42 | 1.922 | Zeta |
| Very weak.... | 27 46 | 1.915 | Fe_3Zn_{21} |
| Very, very weak..... | 28 18 | 1.880 | Fe_3Zn_{21} |
| Very, very weak..... | 28 34 | 1.866 | Unidentified |
| Very, very weak..... | 28 54 | 1.847 | Zeta |
| Very weak.... | 29 24 | 1.818 | Zeta |
| Weak..... | 30 44 | 1.746 | Zeta and Fe_3Zn_{21} |
| Weak..... | 32 3 | 1.682 | Zeta |
| Weak..... | 32 29 | 1.661 | $FeZn_7$ (1.67) |
| Weak..... | 32 52 | 1.644 | $FeZn_7$ (?) (1.626) |
| Weak..... | 34 26 | 1.578 | Zeta |
| Very, very weak..... | 36 19 | 1.506 | $FeZn_7$ (1.518) |
| Weak..... | 36 46 | 1.491 | Fe_3Zn_{21} |
| Strong..... | 38 34 | 1.431 | Fe (200) and Fe_3Zn_{21} |
| Weak..... | 39 14 | 1.411 | Zeta |
| Weak..... | 40 10 | 1.383 | Zeta and $FeZn_7$ (1.393) |
| Very weak.... | 41 9 | 1.356 | Zeta |
| Weak..... | 42 33 | 1.320 | Zeta |
| Weak..... | 42 57 | 1.310 | Fe_3Zn_{21} |
| Very, very weak..... | 43 21 | 1.300 | Fe_3Zn_{21} |
| Medium..... | 44 17 | 1.278 | Zeta and $FeZn_7$ (1.274) |
| Weak..... | 44 50 | 1.266 | Zeta and $FeZn_7$ (1.25) |
| Weak..... | 46 33 | 1.229 | Fe_3Zn_{21} (1.213) |
| Very weak.... | 47 6 | 1.218 | Zeta, Fe_3Zn_{21} , and $FeZn_7$ (1.217) |
| Medium..... | 50 | 1.165 | Fe (211) 1.166 |
| Very weak.... | 56 58 | 1.064 | Zeta |
| Very weak.... | 57 34 | 1.057 | Zeta and Fe_3Zn_{21} |
| Medium..... | 62 2 | 1.010 | Fe (220) 1.01 |

In Fig. 3 a comparison is made of the data of Schramm¹⁰ with the diffraction data from the present sample. Such a chart does not give an accurate check on the work. It permits only a rapid graphic survey of the various phases present.

DISCUSSION OF RESULTS

It is evident from the data in Table 3 and Fig. 3 that all of the intermediate phases of the iron-zinc system are found in the

heat-treated zinc coating. The zeta phase is predominant. Schueler¹ found by chemical analysis that 60 per cent of the heat-treated galvanized coating consisted of a new phase, which he designated $FeZn_{10}$. From the diffraction data presented here and the above fact, it seems evident that the phase found by Schueler and the zeta phase ($FeZn_{13}$) are the same intermetallic compound.

The chemical analysis of the heat-treated zinc coating showed 10 per cent of iron, which is somewhat high for such a coating, the average analysis being about 8 per cent. The homogeneity range of the zeta phase is 6 to 6.2 per cent Fe. A relatively large amount of zeta material would be expected, therefore, the remaining iron being taken care of by $FeZn_7$ (7 to 10 per cent Fe) and Fe_3Zn_{21} (20.5 to 28 per cent Fe).

The phases present in heat-treated zinc coatings have been checked on wire, although the data presented here were obtained from a sheet sample.

SUMMARY

The recent investigations on the iron-zinc system are summarized.

The X-ray diffraction analysis of heat-treated zinc coatings on sheets (and on wire) shows that the alloy layers consist mainly of the zeta ($FeZn_{13}$) phase. Zinc, small amounts of Fe_3Zn_{21} and δ_1 phase are also present in the coating.

The zeta phase corresponds to the phase found by Schueler in 1925.

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DISCUSSION

(P. H. Brace presiding)

P. R. KOSTING,* Watertown, Mass.—It is by no means a simple procedure to use X-ray for the identification of compounds in a complicated mixture. The work of Messrs. Morral and Miller is therefore very interesting and constructive. In the identification of any compound, it is not only necessary to match d values in any pattern, but also to check intensity values. For instance, for iron we anticipate d values around 2.0, 1.4, 1.2, and 1.0, and I values of strong, weak, medium, and weak, respectively. We note on Table 3 that the intensity of the 2.0 line for iron is weak, but the intensities of the 1.2 and 1.1 lines are medium. Similarly for zinc; normally we expect d values of 2.5, 2.3 and 2.1 with corresponding I values of weak, weak, and strong, whereas on Table 3 there is only a medium line corresponding to the 2.1 d value. Traces of the 2.5 and 2.3 line would be expected if the 2.1 line is of medium intensity unless grain size and orientation, etc., interfere. Such discrepancies in the anticipated intensity of lines should be pointed out and satisfactorily explained.

W. D. FORGENG,† Niagara Falls, N. Y.—The authors have mentioned the lack of correlation between the results of Osawa and Ogawa, Stillwell and Clark, and Schramm and other recent German investigators, and at the risk of adding further to the confusion that exists in the X-ray data on the iron-zinc system, and particularly that concerned with galvanized

coatings, I am presenting diffraction patterns and photomicrographs taken at different depths in a dip-galvanized coating. The diffraction patterns in Fig. 5 were taken with filtered cobalt radiation, using the metallographic specimen of Fig. 4. The specimen was polished to increasing depths, and the etched structure recorded. It was then transferred to the X-ray camera, tilted 10° into the X-ray beam, and the diffraction pattern was registered.

The structures shown in the photomicrographs are not necessarily represented by the diffraction patterns, since the X-rays penetrate the specimen to some extent. Some 35 to 60 lines (some too faint to register in a print) are present in each pattern between the limiting θ values of 15° and 65° . While some of the lines could be accounted for on comparison with Schramm's charts in a manner similar to that used by the authors, the agreement was far from satisfactory. Furthermore, an attempt to arrange the lines into a series of patterns by statistical methods required an assumption of at least 11 individual species, giving rise to separate diffraction patterns, whereas only five phases have been recognized microscopically. It is believed that these results can best be explained by the formation of solid solutions between the recognized constituents in the system, which result in a series of related but distinctly different patterns. This would also explain the lack of agreement in the published data referred to in the paper.

F. R. MORRAL (author's reply).—On page 160 the difficulty of evaluating the intensities of lines, particularly on a composite diffraction photogram, is pointed out. We fully realize Mr. Kosting's point; namely, the importance that not only the d values match but also their intensities.

Only the strongest line for zinc ($d = 2.1$; $I = \text{strong}$) showed in the range of our photogram as medium (recorded in Table 3 as $d = 2.09$; $I \text{ medium}$). The other zinc lines that are weak were outside the glancing angle for which the intensities could be estimated with any degree of satisfaction.

Little work (2) has been published on X-ray diffraction analysis of galvanized coatings. It is unfortunate that Mr. Forgeng has not presented the data in more detail with his photomicrographs and the diffraction photograms.

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† Union Carbide and Carbon Research Labs., Inc.

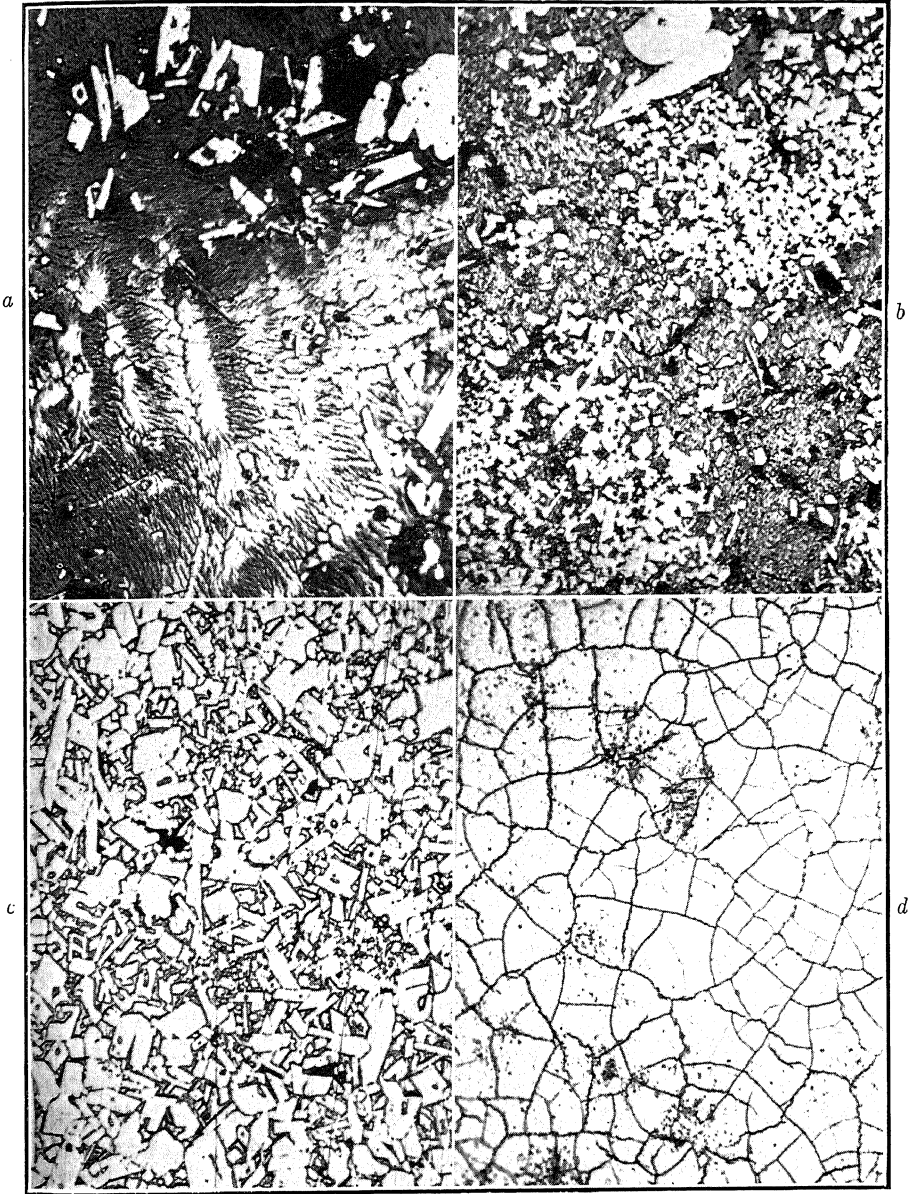


FIG. 4.—DIP-GALVANIZED COATING POLISHED TO DIFFERENT DEPTHS PARALLEL TO STEEL BASE. $\times 250$.

- a*, outside surface (zinc + zeta?).
- b*, adjacent to *a* (zeta + delta + zinc?).
- c*, adjacent to *b* (zeta + delta + capital gamma?).
- d*, layer immediately adjacent to steel base (capital gamma?).
2 per cent Nital etch.

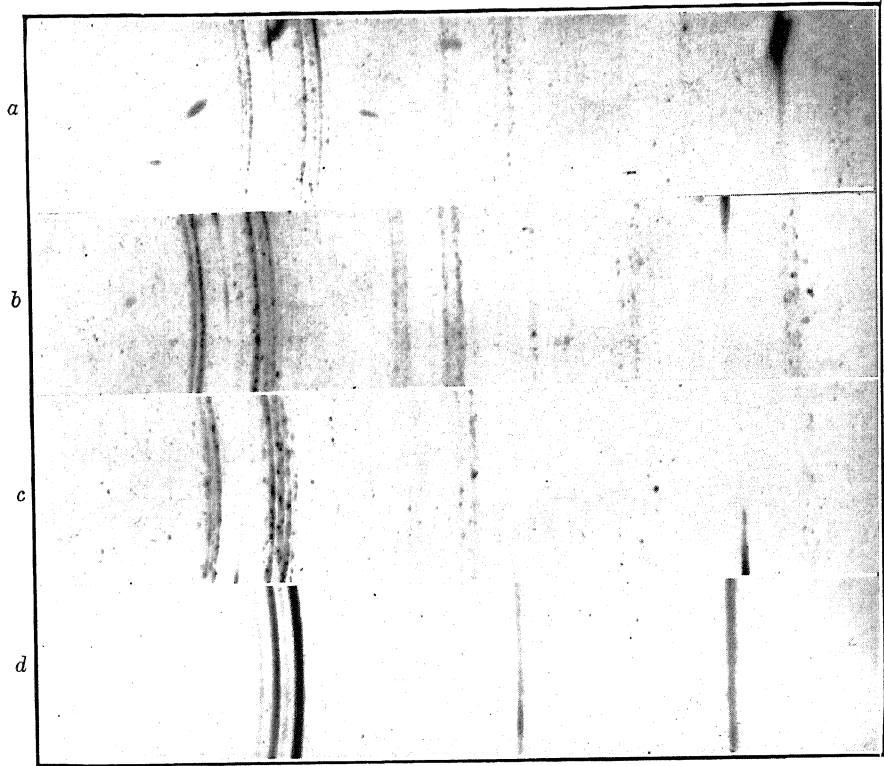


FIG. 5.—DIFFRACTION PATTERNS TAKEN AT GLANCING ANGLE ON SPECIMEN OF FIG. 4. COBALT K_{α} RADIATION.
a, outside surface. b, adjacent to a. c, adjacent to b. d, adjacent to steel base.

TABLE 4.—Comparison of Galvanized Coatings

| | Galvanized | |
|--|------------|-----------------------|
| | Hot Dip | Hot Dip, Heat-treated |
| Weight of coating (approx.), oz. per sq. ft..... | 1.25 | 0.60 |
| Thickness of coating, in..... | 0.001 | 0.0005 |
| Phases by microscopic determination,* per cent: | | |
| FeZn ₁₁ | 18 | 3 |
| FeZn ₇ | 30 | 27 |
| FeZn ₁₈ | 2 | 60 |
| Zn..... | 50 | 10 |

* J. L. Bray and F. R. Morral: Zinc Coatings. Amer. Soc. Metals Preprint 45 (1940). Symposium on Surface Treatment.

A regular hot-dip galvanized coating differs from the coating discussed in the paper in several respects (Table 4).

Mr. Forgeng's photomicrographs show well that these alloys are not evenly distributed in one layer but actually overlap. This effect, together with the penetration of the X-ray beam, causes the diffraction of more than one phase on the photographic plate. When two or more phases are formed on a photographic plate, the intensities present depend on the relative amounts of the phases present. This may account for the difficulty in making his data agree with those of Schramm. In addition, when two or more phases are present together, one of them may be slightly displaced.

Creep and Recrystallization of Lead

BY ALBERT A. SMITH, JR.,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1940)

THE creep properties of metals have assumed increasing importance in recent years and many investigations have been made on various phases of the problem. In the past year the annual lectures of the Institute of Metals Division¹ and the Iron and Steel Division² were concerned with this subject, and are excellent reviews. For many years the creep properties of lead and lead alloys have been investigated at the Central Research Laboratories of the American Smelting and Refining Co., and it is hoped that the present paper will contribute knowledge of some of the factors that influence creep. Lead, being a metal that recrystallizes readily at room temperature, is an excellent material upon which to investigate creep phenomena because of the simplicity of the apparatus needed, and it might be expected that results would apply to some extent to elevated-temperature tests of other metals.

MATERIAL

The creep tests of this investigation were all made on high-purity lead (99.9998+ Pb) in which the only impurity that could be detected by spectrographic and chemical means was approximately 0.0001 per cent Fe. Flat strips, 0.750 in. wide by 0.100 in. thick, were prepared by extruding 2-in. dia. cast billets at a temperature of 250°C. This gave a material of 2 to 3 mm. average grain size with a tensile strength of 1400 lb. per sq. in. when tested at a straining rate of 5

per cent per minute. With this extremely soft material, great care was necessary in handling the specimens, to avoid distortion and subsequent recrystallization.

APPARATUS

The creep tests at 30°C. were conducted in a constant-temperature room, specially built for the purpose in the basement of an office building in which there was no moving machinery, and no vibration was detectable under the most severe conditions of shock in the adjacent surroundings. The room was well insulated and heated electrically, control being by means of a de Khotinsky regulator operating a relay. Maximum temperature variation over a period of several years has been $\pm \frac{1}{2}^{\circ}\text{C}$.

Specimens of the extruded strip, 16 in. long, were used for test purposes with no reduced gauge section, thus eliminating any distortion due to machining. The method of clamping and supporting the specimens is shown diagrammatically in Fig. 1.

The gauge marker for the measurement of extension consisted of an aluminum strip, 0.050 in. thick by 0.75 in. wide, one end of which was ground and sanded to a precise knife-edge and fastened to the specimen by suitable pins. After the strip was fastened in place a fine scratch was inscribed just below the knife-edge by means of a sharp teasing needle. Just below this gauge scratch a short vertical mark was made so that the same point could be located and read each time. Several hundred specimens have been prepared by this method, and it was found that with experi-

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* Research Metallurgist, American Smelting & Refining Co., Barber, N. J.

¹ References are at the end of the paper.

ence excellent gauge marks could be made. As far as could be ascertained by careful observation, no shifting of the aluminum strips has taken place over test periods up to three years.

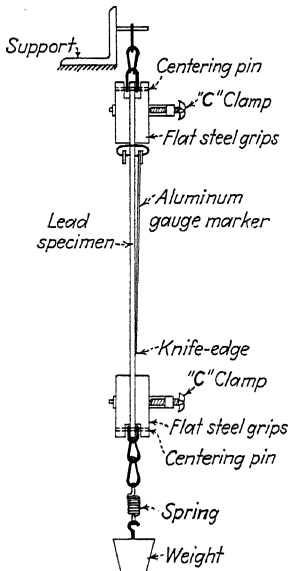


FIG. 1.—SPECIMEN ASSEMBLY.

Strain measurements were made by determining the distance between the lower edge of the aluminum strip and the fine scratch inscribed on the lead specimen by means of a portable micrometer microscope sensitive to 0.000025 in. Actually the limit of sensitivity depended upon the fineness of the cross scratch on the lead specimen and it is estimated that the accuracy was at least 0.0005 in. Since the gauge length was 10 in., this gave a minimum accuracy of 0.00005 in. per inch.

The tests at 55°C. were conducted in an electrically heated, thermostatically controlled oil bath, which contained 12 test stations. In a tank 4 in. wide, 86 in. long and 22 in. high, with a glass front, clear transformer oil was used, through which readings could be made with the microscope. The specimens were connected at the bottom to an angle beam welded to the tank. Loading was accomplished by tak-

ing the load out at the top of the tank by means of a lever arm with a one to one ratio. Readings were secured by the use of aluminum markers in the same manner as described above for the 30°C. tests.

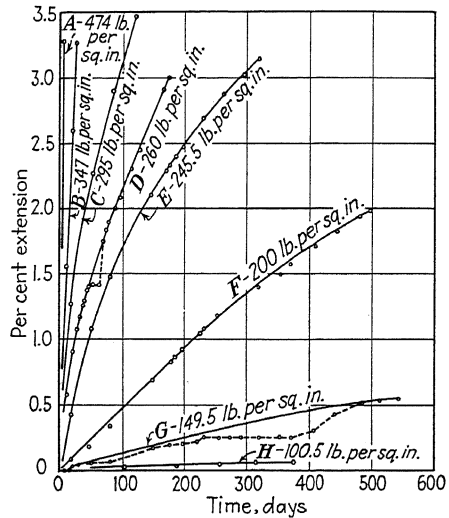


FIG. 2.—CREEP AT 30°C.

Exceptionally good temperature control was maintained in the tank, variation being only about $\frac{1}{4}$ °C. at the maximum.

A similar tank was used for the 100°C. tests but air heating was employed because the oil discolored at this temperature to such an extent that readings could not be made. Air, preheated externally by resistance heaters, was circulated at high velocity through the tank to secure as uniform heating as possible. The temperature variations with this tank were about ± 4 °C.

DATA

Time-extension curves for the 30°C. tests are plotted in Fig. 2, and it is apparent that in some cases creep does not proceed at a uniform rate but rather by intermittent steps. Curve G is particularly interesting on this point. For the first 15 days of the test there was no discernible motion (less than 0.005 per cent) but the next reading, at 18 days, showed 0.025 per cent extension. The extension proceeded somewhat irregularly

for 231 days and then for a period of 140 days there was no further motion. At 371 days the specimen again started to elongate, the rate accelerating for a time and then

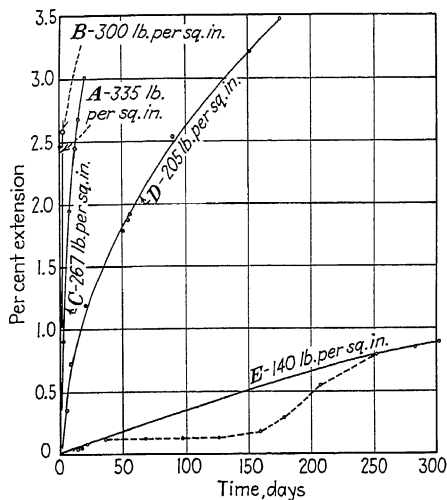


FIG. 3.—CREEP AT 55°C.

decreasing. Obviously, it is difficult to determine creep rates from these stepped

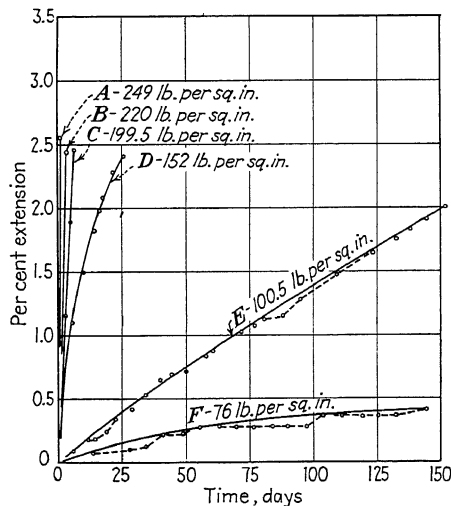


FIG. 4.—CREEP AT 100°C.

curves, but a smooth curve can be drawn through the high points as shown by the solid line of curve G.

Figs. 3 and 4 show time-extension curves for 55° and 100°C. of other specimens at low stresses, which are also of the step type and on which smooth curves can be drawn

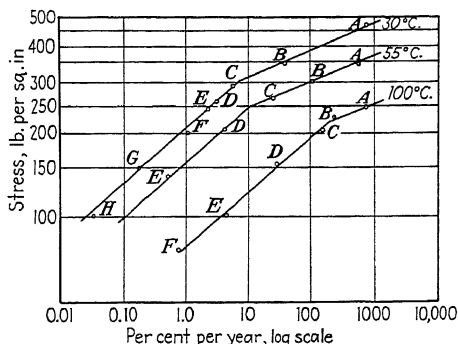


FIG. 5.—LOG-RATE LOG-STRESS CURVES.

through the high points as shown by the solid lines. Chronologically there was no relationship between the various specimens as to the time when rapid motion would take place. It is evident that a sudden shock should affect in the same manner two adjacent specimens suspended from the same angle support, nor can this explain long periods of zero extension. From this evidence and from examination of creep data from hundreds of other tests, it is believed that creep may occur intermittently and that the periods of rapid and slow extension take place at random. Also, it is very probable that any vibration superimposed on the tensile stress may produce a more uniform type of elongation.

If the minimum creep rates obtainable from the time-extension curves are plotted on a log-rate log-stress scale as in Fig. 5, continuous lines are obtained for each of the three temperatures. At the higher stresses, there are changes of slope of the curves, indicating a higher rate of extension than might be expected by extrapolation from the low stress region. Microscopic examination of the specimens corresponding to the high-stress part of the curve was made immediately before and after the creep tests, and it was found that partial or com-

plete recrystallization had taken place. The resulting grain size, after deformation of about 3 per cent, was 5 to 20 times as large as the original grain size, so that there was

To confirm this point, a new specimen (curve *D* of Fig. 2) was carefully etched and then a crosshatch of very fine lines spaced about $\frac{1}{8}$ in. apart was inscribed on one flat



FIG. 6.—CREEP SPECIMEN.

a, original etch; *b*, same area re-etched. $\times 50$.

little question that the specimens had recrystallized during the test. On the other hand, specimens C and E at 30°C., D and E at 55°C., and C, D and E at 100°C., corresponding to the low-stress region, showed no change in grain size and it is doubtful whether any recrystallization had taken place.

The specimen was then loaded at a stress of 260 lb. per sq. in. and creep readings were made. In 171 days the specimen extended 3 per cent and this particular curve shows a period of about 10 days in which there was practically no motion and then a rapid extension of 0.35 per cent in 7 days, after

which the extension proceeded as though no halt had occurred.

After the test was completed various parts of the surface of the specimen were

original grain structure was still present with no evidence of recrystallization.

In order to determine the time necessary to produce recrystallization at 30°C. by

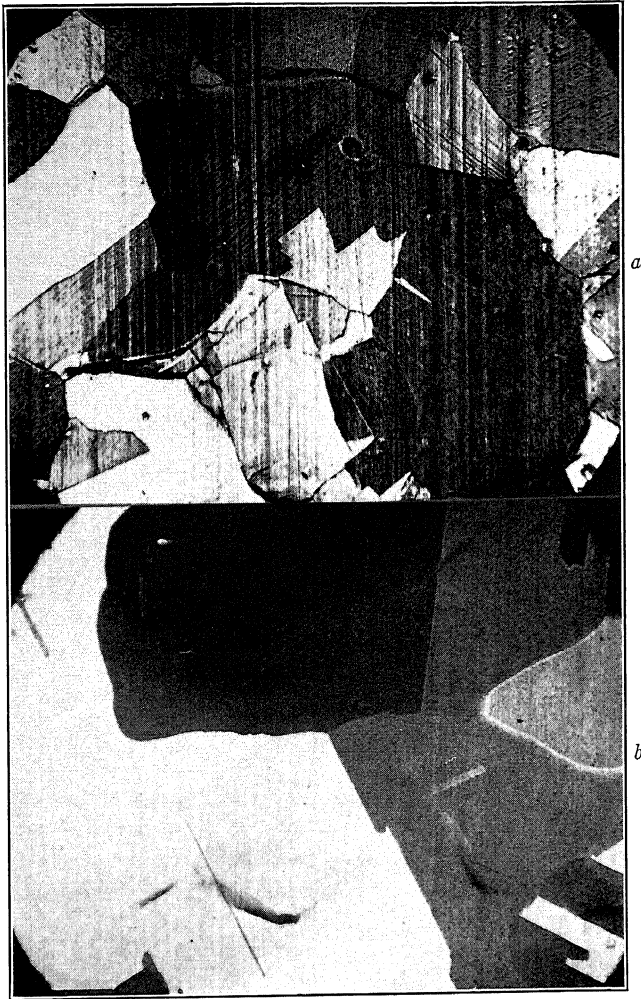


FIG. 7.—TENSILE SPECIMEN.
a, original etch; *b*, same area re-etched. $\times 50$.

photographed with the original etch, and one of these photographs is shown in Fig. 6*a*. Four weeks after the completion of the creep test the surface was heavily re-etched, the region previously photographed was relocated by counting the cross lines and photographed again. Fig. 6*b* shows that the

straining in tension, samples from the strip adjacent to those used for creep tests were extended 1 and 3 per cent in a testing machine at a rate of 5 per cent per minute. From microscopic examination, it was found that the sample extended 3 per cent completely recrystallized in about one hour.

Fig. 7a shows the sample immediately after straining and Fig. 7b shows the same area after recrystallization had taken place. It is evident that there is a decided difference in the grain size produced by the small deformation. The sample that was extended

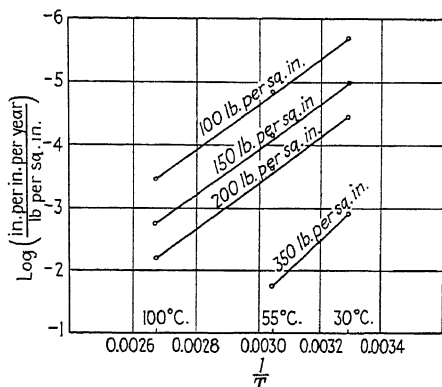


FIG. 8.—DATA ON PURE LEAD.

1 per cent recrystallized in about 10 days and the resulting grain size was somewhat larger. The photograph of the creep specimen, Fig. 6, was taken four weeks after the test had been completed and four months later there was still no visible change in the grain structure.

It is therefore concluded that the low-stress section of the curves of Fig. 5 represents creep with very little or no strain of the type that produces recrystallization, whereas the higher creep rates, corresponding to the high-stress section of the curves, are accompanied by recrystallization.

The photomicrographs show many slip (or deformation) bands, although unlike normal slip lines even the extremely deep re-etching, which produced many pits, did not completely eliminate them. In some cases these bands became curved as they neared grain boundaries. This particular phenomenon has been noted by Hanson and Wheeler³ on creep specimens of aluminum and they suggest that the bands are determined by maximum shear stresses rather than by crystallographic directions.

DISCUSSION OF RESULTS

The creep data presented show that creep does not necessarily take place in a smooth, continuous manner, but may be intermittent, with periods of rapid and slow extension. There does not appear to be any relationship between time or amount of extension relative to the occurrence of these steps; apparently they take place at random. Recrystallization is not necessarily a factor,⁴ as none could be detected except at comparatively high rates of extension, whereas the steps occur mainly at low rates. Considering the high purity of the lead used, any strain-aging phenomenon must be excluded. In a recent discussion⁵ based upon the ideas of Orowan⁶ it was suggested that the occurrence of stepped creep curves is determined by the simultaneous effects of stress concentration and thermal agitation. At some certain time a locally concentrated stress is further increased by the haphazard thermal stress fluctuations in the lattice and sudden elongation results. It was postulated in the discussion at that time that steps in the creep curves might be larger if very pure materials and lower temperature and stresses are used. In general this has been found to be true and these data indicate that at 100°C. the steps are less pronounced. Another point observed in the study of the creep of lead is that the steps also tend to become less pronounced with decreasing grain size.

The change in the slope of the stress-rate curves of Fig. 5 is of considerable interest and has been noted by other investigators,^{7,8} who refer to it as the change from plastic to viscous flow. The present results indicate that a major difference between the two regions is the presence or absence of recrystallization. At the high rates of extension, creep is accompanied by recrystallization. At the low rates the deformation appears to be confined in a large degree at or near the grain boundaries, although there is considerable internal deformation, as the

photomicrographs indicate. However, the mechanisms of both the grain boundary and internal deformation are of such a nature that recrystallization does not occur. As the temperature decreases, the creep rate at which the transition from one type of flow to the other occurs also decreases.

Kanter⁹ has proposed an energy analysis of the creep process from which an energy value can be calculated that is of the same order of magnitude as the heat of diffusion of the metal. He plots the log flowability $\left(\frac{\text{rate}}{\text{stress}}\right)$ versus the reciprocal of the absolute temperature, and from the resulting straight lines computes an energy value that is approximately equal to the heat of diffusion.

The data on pure lead are plotted in this manner in Fig. 8, the upper three lines for 100, 150 and 200 lb. per sq. in. being from the low rate part of Fig. 5 and the other curve for 350 lb. per sq. in. from the high rate portion. In the first instance an energy value of 16,500 cal. per gram mol is obtained and for the other case a value of 21,000 cal. per gram mol. The accepted value of the heat of self-diffusion of lead is 28,000 cal. per gram mol,¹⁰ which is considerably different from the value computed from the low-creep-rate data. The value from the high rate of extension is more nearly comparable but this is at a rate where spontaneous recrystallization takes place and the process cannot be closely related to diffusion.

CONCLUSIONS

1. The creep properties of high-purity lead have been determined at temperatures of 30°, 55° and 100°C.
2. It has been shown that creep of lead does not necessarily proceed uniformly but may take place in intermittent steps.
3. At comparatively high rates of extension recrystallization occurs while at lower rates none could be detected. When recrystallization is a factor, the creep rates are

greater than would be obtained by extrapolation from the low rate part of the log-rate log-stress curve.

4. Employing the method proposed by Kanter, an energy value of 16,500 cal. per gram mol is obtained that is considerably different from the value for the heat of self-diffusion of lead.

ACKNOWLEDGMENT

The author is indebted to Dr. A. J. Phillips, under whose direction this work was done, and to Mr. P. A. Beck, for their helpful suggestions in preparing this paper.

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2. H. W. Gillette: *Trans. A.I.M.E.* (1939) 135, 12.
3. Hanson and Wheeler: *Jnl. Inst. Metals* (1931) 45, 229.
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9. J. Kanter: *Trans. A.I.M.E.* (1938) 131, 385.
10. Seith and Keil: *Zisch. Metallkunde* (1933) 25, 104.

DISCUSSION

(B. B. Betty presiding)

J. J. KANTER,* Chicago, Ill.—The data offered by Dr. Smith upon the creep characteristics of pure lead are of considerable theoretical interest. It seems reasonable that at the small loads and slow rates of creep, the strain curve need not be smooth, in view of the coarse-grained material used. It may well be that the strain accumulates intermittently through two types of movement, one associated with the grain boundaries; the other with slip planes.

In connection with Fig. 8, it is of interest to consider the data of Hanfstengel and Hanemann represented in the accompanying diagram (Fig. 9), where a constant strain rate at 70.4 lb. per sq. in. is represented as a function of a reciprocal of the absolute temperature. An energy value of 13,500 cal. per gram mol is deduced from these data and compares favorably with the 16,500 cal. per gram mol from Dr. Smith's data. Incidentally, it might be mentioned that had Dr. Smith plotted log rate of strain vs. reciprocal of absolute tempera-

* Crane Company.

ture, instead of log flowability, the energy value so deduced would be identical with that from Fig. 8. Since, for the data under consideration, stress enters into the calculation of each curve

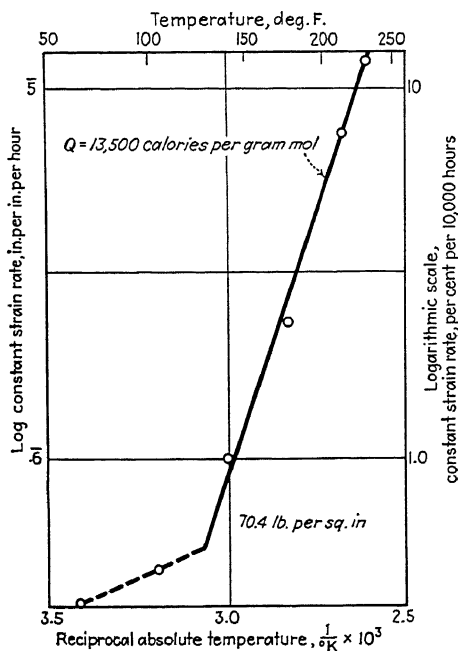


FIG. 9.—RECIPROCAL ABSOLUTE TEMPERATURE PLOT OF HANFFSTENGEL AND HANNEMAN CREEP DATA FOR SOFT LEAD UNDER A STRESS OF 70.4 LB. PER SQUARE INCH.

Drawn from data found in paper by K. von Hanffstengel and H. Hanneman: Mechanism of Creep and Fatigue Limit Investigated on Lead and Lead Alloys. *Ztsch. Metallkunde* (1937) 29(2), 50-52.

as a constant term, the only advantage for the log-flowability scheme is if a constant stress curve is to be deduced from data involving a variety of stresses where it is necessary to find a stress function that will permit the data to be compared at picked constant stress values.

The fact that the energy value deduced in the data falls short of the heat of self-diffusion for lead possibly is still reconcilable with the idea that some aspects of creep are akin to solid diffusion. It still may be contended that this energy value is of the order of magnitude of the heat of self-diffusion. When one takes into consideration the fact that the crystal movement associated with this value is largely in

the locale of grain boundaries, it would seem that the restraints upon a process of solid diffusion so taking place would be appreciably less than solid diffusion through an orderly space lattice. A grain-boundary atom might be considered to belong almost as much to the adjoining crystal as to the parent crystal, and thus the activation energy necessary to promote its migration would seem far below that necessary to promote the migration of an atom buried in the space lattice. Possibly the fact that our activation energies for lead, deduced from both Dr. Smith's data and the Hanffstengel and Hanneman data, turned out to be approximately half of that found for the heat of self-diffusion, is quite significant with respect to the well-known fact that the finer the grain structure associated with a metal, the higher its creep rate at a given stress above the temperature for recrystallization.

W. H. BASSETT, JR.,* Hastings-on-Hudson, N. Y.—The data obtained in our laboratories on common desilverized and copper lead, when using an entirely different test method from the one described by Dr. Smith, agree with the results reported by the author.

The samples used in our laboratory consisted of 15-in. lengths of extruded pipe approximately $2\frac{3}{4}$ in. o.d. by $\frac{1}{8}$ in. thick. The ends of the pipe were sealed by means of hollow plugs. The pipe was filled with oil, then hydraulic pressure was applied by means of a pump and accumulator, so that the samples were kept at constant pressure until failure occurred. By taking gauge measurements we were able to determine the rate of expansion of the tubes while determining the length of time required for rupture of the wall. Specimens were tested over a fairly wide range of time intervals and pressures. Rather high internal pressure caused failure in only 5 min. while at lower pressures the pipe lasted over 2 years before rupture occurred.

Fig. 10† shows a sample of pipe and the method of plugging the ends. Fig. 11 shows samples of burst pipe and indicates the type of fracture and the variation of expansion noted. Some lead alloys expand to a considerable extent while others give very little expansion

* Manager, Metallurgical Department, Anaconda Wire and Cable Co.

† Figs. 10-13, 15, 17, 19, 21 were used in the paper by W. H. Bassett, Jr. and C. J. Snyder: *Proc. Amer. Soc. Test. Mat.* (1940) 40, 910-936.

before bursting. The conditions reported by the author as to specimens apparently showing no creep for a considerable period of time and then making a sudden change in dimensions was

formation of fine grains at the grain boundaries. Fig. 16 shows the structure of the same sample 17 months after rupture. The fine grains are still noticeable at the grain boundaries. Fig. 17

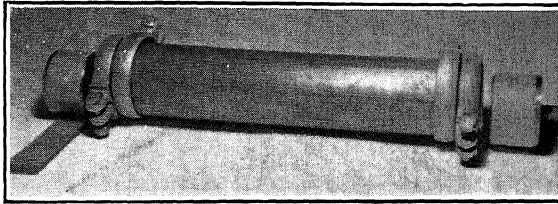


FIG. 10.—SAMPLE OF PIPE WITH PLUGGED ENDS.

also noted in the tests of the extruded pipe. Fig. 12 shows a group of typical curves drawn from the data obtained on various lead-pipe specimens. The samples used for this figure were common desilverized lead, chemical lead, copper lead and calcium lead. Two different specimens of copper lead are shown—one sample from a tube and the other from a cable sheath. The extra working of the metal during the sheathing operation gives an entirely different shape of curve and materially increases the life of the sample. Fig. 13 shows a summation of data obtained on various grades of lead and lead alloys as to the time required to burst the specimens when subjected to various internal pressures. Table 1 shows the composition of samples used in the preceding figures. Fig. 14 shows a cross section of common lead pipe before test. The ring picture in the center shows a complete cross section and the enlargements show the structure of the top and bottom weld area and of the respective sides of the pipe. This pipe was subjected to 600 lb. per sq. in. hoop stress and burst after 2 months. Fig. 15 shows the structure of the specimen one day after rupture occurred. Note the

shows the structure of a copper lead pipe before test. This sample was subjected to 800 lb. per

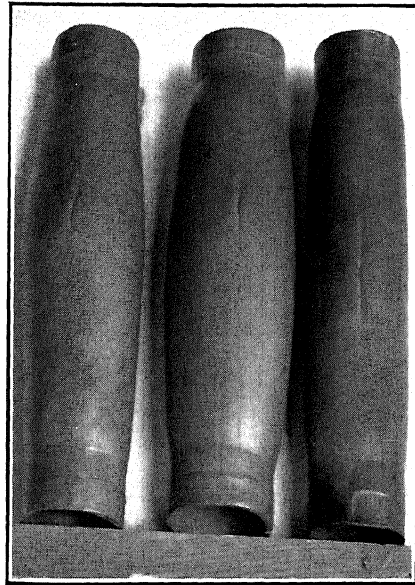


FIG. 11.—SAMPLES OF BURST PIPE.

TABLE 1.—*Chemical Analyses of Burst Test Specimens*
PER CENT

| Sample No. | Lead | Bismuth | Copper | Anti-mony | Tin | Silver | Tellurium | Nickel | Calcium | Magnesium |
|------------|--------|---------|--------|------------------------------------|-------|---------|-----------|--------|---------|-----------|
| 2264 | 99.920 | 0.065 | 0.013 | 0.0015 | 0.000 | | | | | |
| 2261 | 99.921 | 0.066 | 0.011 | 0.0015 | 0.000 | | | | | |
| 2180 | 99.880 | 0.059 | 0.059 | 0.002 | 0.000 | 0.0010* | | | | |
| 2181 | 99.884 | 0.057 | 0.057 | 0.002 | 0.000 | | | | | |
| 2747 | | | | (Similar to Samples 2180 and 2181) | | | | | | |
| 2758 | 99.826 | 0.100 | 0.072 | 0.001 | 0.000 | 0.0015 | 0.000 | 0.000 | | |
| 2296 | 99.925 | 0.000 | 0.065 | 0.0003 | 0.000 | 0.005* | | 0.0044 | | |
| 2445 | 99.778 | 0.126 | 0.059 | 0.004 | 0.000 | 0.013 | 0.020 | | | |
| 1228 | 99.905 | 0.000 | 0.053 | 0.0007 | 0.000 | 0.0062 | 0.000 | 0.0044 | 0.031 | |
| 2856 | 99.658 | 0.019 | 0.005 | 0.002 | 0.26 | | | | 0.025 | 0.031 |

* Nominal average.

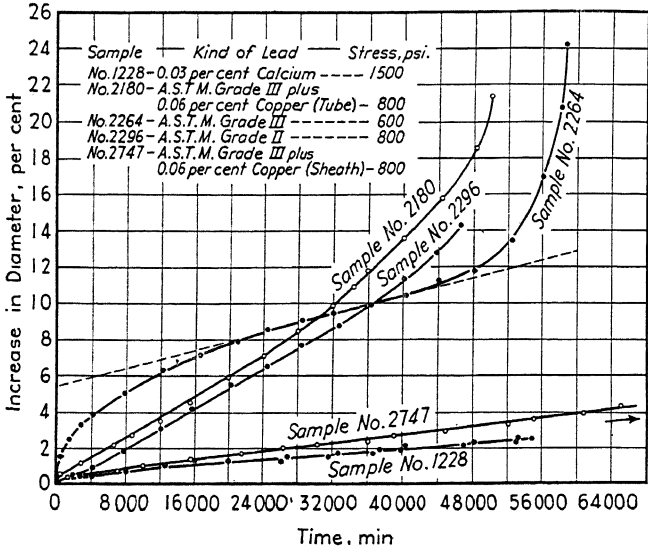


FIG. 12.—TYPICAL CURVES FROM DATA ON LEAD-PIPE SPECIMENS.

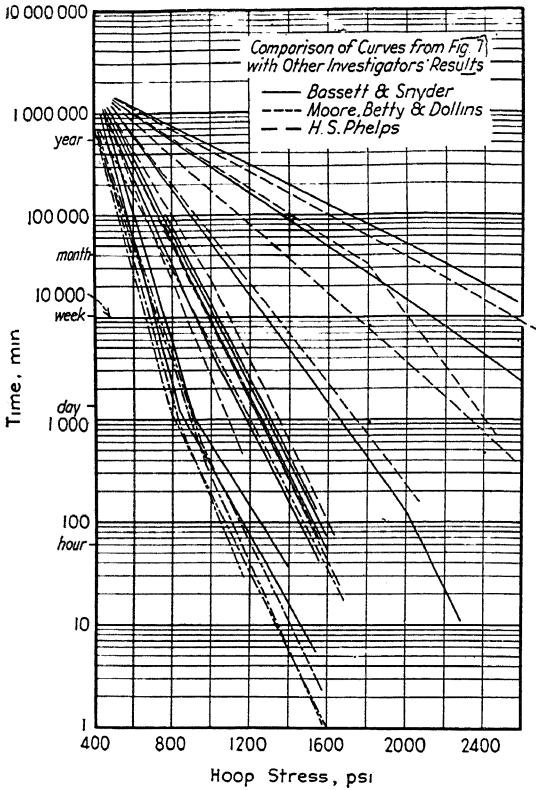


FIG. 13.—DATA REGARDING TIME REQUIRED TO BURST SPECIMENS SUBJECTED TO INTERNAL PRESSURE.

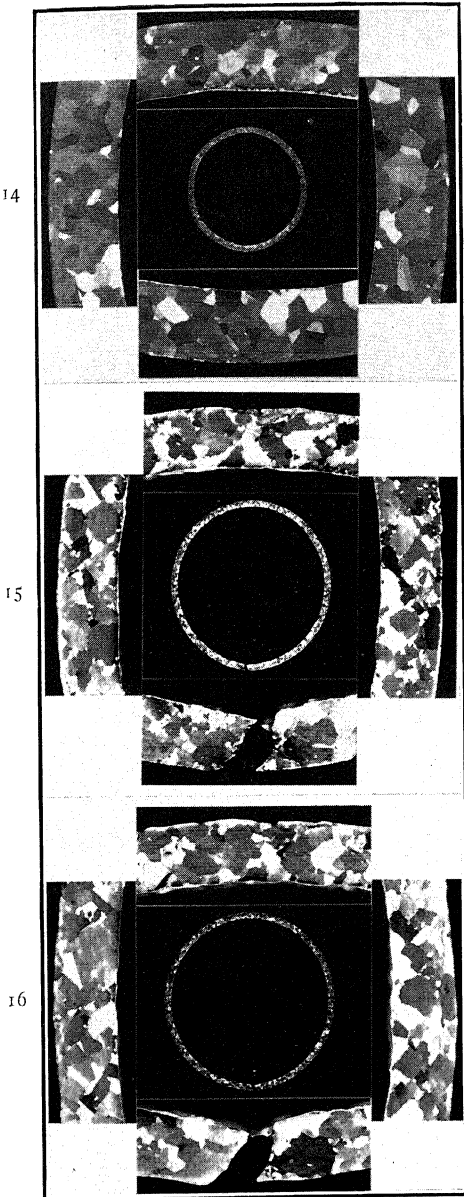


FIG. 14.—CROSS SECTION OF COMMON LEAD PIPE.

FIG. 15.—STRUCTURE OF SPECIMEN OF FIG. 14 ONE DAY AFTER RUPTURE.

FIG. 16.—STRUCTURE OF SAME SAMPLE SEVENTEEN MONTHS AFTER RUPTURE.

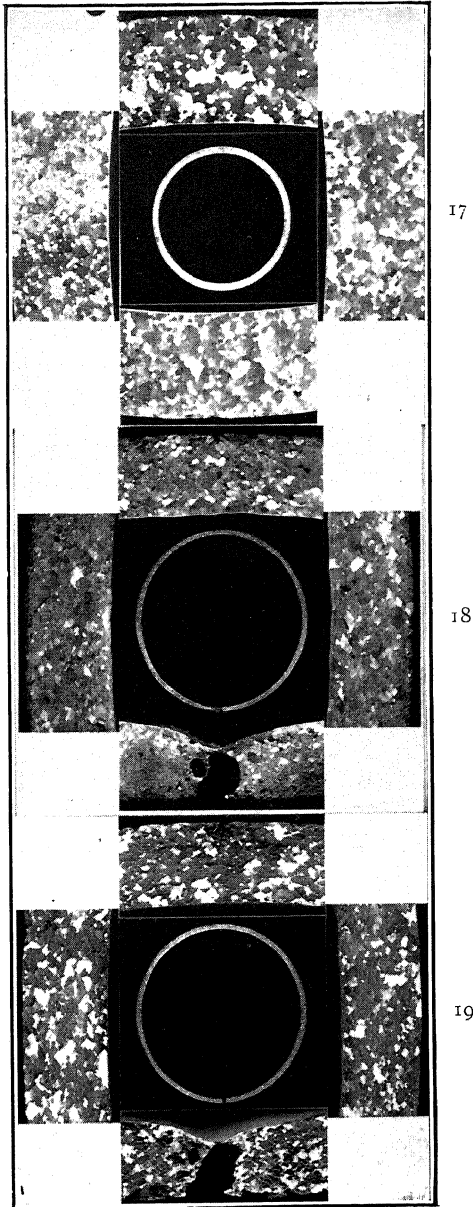


FIG. 17.—STRUCTURE OF COMMON LEAD PIPE BEFORE TEST.

FIG. 18.—SAMPLE OF FIG. 17 TEN WEEKS AFTER SPECIMEN BURST.

FIG. 19.—SAME SAMPLE TWENTY-SIX MONTHS AFTER SPECIMEN BURST.

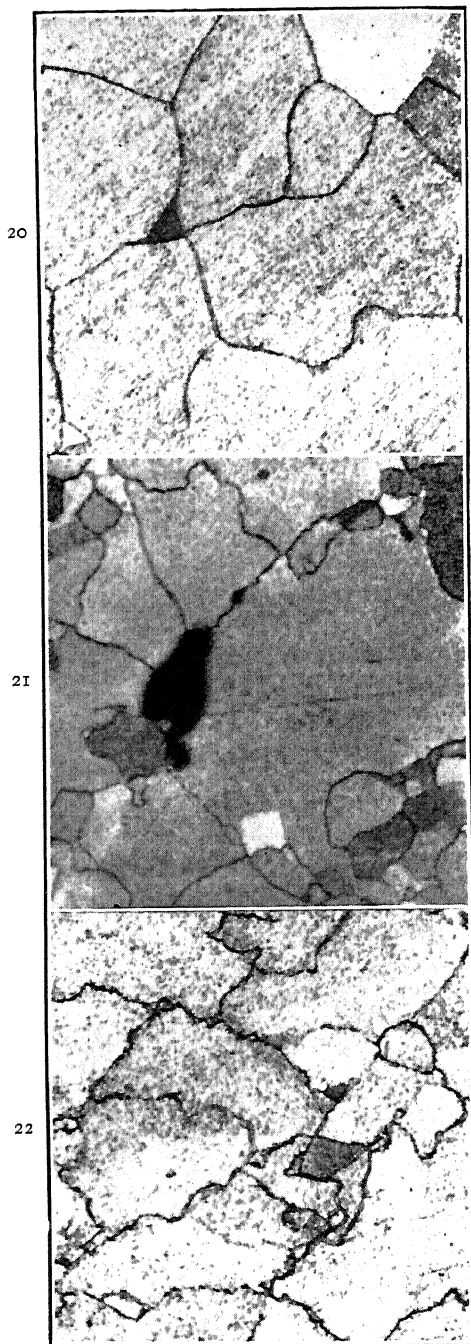


FIG. 20.—STRUCTURE OF ORIGINAL COPPER-LEAD SAMPLE BEFORE TEST. $\times 100$.

FIG. 21.—SAMPLE OF FIG. 20 TEN WEEKS AFTER FAILURE. $\times 100$.

FIG. 22.—SAME SPECIMEN TWENTY-SIX MONTHS AFTER FRACTURE. $\times 100$.

sq. in. hoop stress and burst after 2 months. Fig. 18 shows the structure of the sample 10 weeks after the specimen burst. There is a marked change in the crystal structure. Fig. 19 shows the same specimen 26 months after the specimen burst. Fig. 20 shows the structure of the original copper-lead sample before test, at a magnification of 100 diameters. Fig. 21 shows this copper-lead sample 10 weeks after failure. At 100 diameters the small crystals at the grain boundaries and the irregular shape of the grain boundaries is readily noted. Fig. 22 shows the same specimen 26 months after fracture occurred. The small crystals can still be noted between the grain boundaries and the wavy appearance of the crystal grain boundaries is very noticeable.

The similarity of results obtained by the author on high-purity lead with flat strips and the results we obtained with extruded pipe from the commercial grades of lead would seem to indicate that the author's conclusions can be expanded to cover a broader range of material.

E. E. SCHUMACHER,* New York, N. Y.—The irregular shape of the time-elongation curves as reported here and by others for the specimens tested at low stress is extremely interesting. There seems to be general agreement among those who have published data on creep that this irregularity is most pronounced in low stress tests on lead of quite high purity and in specimens having large grain size. Many investigators have observed that extension of lead alloys under loads causing creep may take place by grain deformation, by grain-boundary separation which leaves voids in the material, or by motions of the grains relative to each other along the boundaries.

A possible explanation for the irregular creep rates reported by Dr. Smith may be given for those instances where the grain size is large and the stress is low. Under these conditions it is probable that the last-mentioned mechanism of extension is dominant. In a sample containing a random grouping of grains of various shapes, sizes and orientations it is reasonable to suppose that some configurations are much more favorable than others to motion along the grain boundaries. After a certain amount of motion there will have occurred some rotation until irregularities interlock and prevent further motion. Additional extension of the specimen

* Bell Telephone Laboratories.

would then have to take place by slip within the grains themselves, which, at the low stresses employed, would take place slowly. This mechanism, after a period of time, would once more bring some grains by rotation into positions favorable to intergranular motion and again permit extension of the specimen.

This explanation of the irregular creep rate is consistent with the observation of the author that coarse-grained materials flow at more irregular rates at low creep stresses than fine-grained materials. In the latter case, individual instances of unfavorable orientation between grain neighbors would have a less pronounced effect on the creep rate of a specimen as a whole.

R. L. TEMPLIN,* New Kensington, Pa.—I realize the space limitations imposed on authors of a paper such as this, yet, in view of our own experience in conducting creep tests and the brief description given by the author of his apparatus and test procedure, I would like to ask what precautions were taken to make sure that his creep tests were free from vibration effects. The schematic drawing of the specimen assembly shown in Fig. 1 does not clearly indicate the details of the support used for each specimen. While the author states that "no vibration was detectable under the most severe conditions of shock in the adjacent surroundings," no details are given of how he assured himself of this fact. Under conditions of instability that must occur during a creep test, it would seem logical to expect that vibration might under suitable conditions cause irregularities in the creep curves similar to some of those shown in the data presented by the author.

B. B. BETTY,† Huntington, W. Va.—In connection with the question of possible effects of vibration on rates of creep, two facts offer considerable comfort to the laboratory worker. In a cooperative investigation to test the reproducibility of creep rates on K-20 steel, a number of different laboratories in different parts of the country obtained almost identical creep curves. It seems safe to presume that they were subjected to different intensities of vibration and hence ordinary vibration resulting from street traffic probably has little

deleterious effect on creep tests. Secondly, in a single laboratory, specimens in adjacent creep frames may have pulsating creep rates whose undulations are not in phase; i.e., their maximum rates do not occur simultaneously. The argument often advanced to explain this pulsating creep rate phenomenon, that it is due to vibrations, does not seem to be sufficient. If the cause of this cyclical effect is to be attributed to shock, a second assumption is necessary; namely, that the metal varies from time to time in its responsiveness to shock waves.

A. A. SMITH, JR. (author's reply).—Although the energy value deduced from the data falls short of the heat of self-diffusion for lead, there still may be some relationship between creep and diffusion as suggested by Dr. Kanter. However, the relationship is probably very complex and such factors as grain size, rate of deformation and recovery must be considered. As the paper indicates, if the rate of creep is low the type of deformation produced does not cause recrystallization; that is, recovery proceeds at such a rate and in such a manner as to offset the lattice distortion. This recovery process probably is due to some type of atomic movement, but whether it may be of the same nature as self-diffusion is not entirely clear from our present knowledge.

The data given by Mr. Bassett on burst tests of various brands of lead tend to confirm the author's findings that in long-time tests no recrystallization can be found.

Mr. Schumacher has put forth a very interesting suggestion regarding the irregular shape of the time-elongation curves and in some instances it may explain the phenomenon. However, when there are long periods of zero extension, it is difficult to understand how the grains can be rotated into more favorable positions for further extension. It is conceivable that during these waiting periods certain obstructions to further motion are relieved by the thermal vibration of the atoms. This idea appears consistent with the data relative to the lack of recrystallization at low creep rates, which probably is due to some recovery effects in the specimens.

Undoubtedly, the presence or absence of vibration during creep testing is an important factor, as Mr. Templin suggests and under

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† Research Laboratory, International Nickel Co.

suitable conditions might cause irregularities in the creep curves. In the same creep room where lead is being tested there are copper alloy wires of 60-in. gauge length under test and many hours spent observing these specimens with a microscope have failed to show any vibration despite the high accuracy of measurement. Moreover, as mentioned in the paper it is evident that a sudden shock should

affect in the same manner two adjacent specimens suspended from the same angle support, nor can this explain long periods of zero extension.

Other laboratories have also noted this type of creep curves and Mr. Betty's remarks confirm the author's belief that vibration does not appear to be sufficient to explain the pulsating creep phenomenon.

Tensile Properties of Rolled Magnesium Alloys—Binary Alloys with Calcium, Cerium, Gallium, and Thorium

By JOHN C. McDONALD,* JUNIOR MEMBER A.I.M.E.

(Cleveland Meeting, October 1940)

THIS report is a continuation of an earlier one with a similar title,¹ to which the reader is referred for such details of procedure as do not appear here. A brief summary will be given of the objects and methods of the research at this time.

It was pointed out in the previous paper that properties of magnesium alloys, as reported by different workers, often differ. This was thought to be due to differences in the preparation of the specimens tested. The ideal way to compare alloys would be to prepare each of them in so many ways that reasonable assurance would exist that the best properties of each alloy had been developed. The alloys would then be compared on the basis of these properties.

The treatment actually given the alloys of these studies is necessarily a compromise with completeness. Nevertheless, enough treatments have been given so that a considerable degree of assurance exists that the properties obtained are representative of the alloy as such, and not merely of the manner in which it was worked and heat-treated.

PROCEDURE

The alloys were cast in the form of cylindrical ingots, which were extruded into bar before being rolled. Some of the ingots were made in 2-in. diameter molds whereas all of the alloys of the previous paper were cast in 4-in. molds. For the larger ingots,

the extruded bar was 2 by 0.140 in.; for the 2-in. ingots, it was 1 by 0.100 in. Preliminary work indicated that strip rolled from both sizes of the bars would have substantially the same properties.

The bar was rolled at some temperature in the range 400° to 800°F., for a total reduction of 50 per cent. The temperature and reduction per pass were so selected that no cold cracking occurred, but were such as to leave the metal in a semihard condition. The hot-rolled metal was annealed at several temperatures in the range 400° to 800°F.; it was also cold-rolled, and given solution and aging treatments. Two standard test bars corresponding to each treatment were pulled in tension, and the average was obtained. Twelve treatments, in all, were given each alloy.

The properties of the annealed specimen having the highest percentage of elongation were selected to represent the alloy in the annealed condition. The properties of the cold-rolled specimen having the highest yield strength were selected to represent the alloy in the cold-rolled condition. These properties were then plotted against percentage composition by analysis. Smooth curves were drawn among the points, thus graphically averaging the results over the entire range studied. The percentage of elongation in the cold-rolled state was not plotted, since it was always low, and varied in an irregular manner with composition.

ALLOYS STUDIED

Magnesium-calcium Alloys.—Fig. 1 presents the results on the alloys of the mag-

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* The Dow Chemical Co., Midland, Michigan.

¹ References are at the end of the paper.

nesium-calcium system. There is a rapid rise in ductility up to 0.1 per cent Ca, which is maintained to 0.3 per cent Ca, after which it slowly decreases. The rise

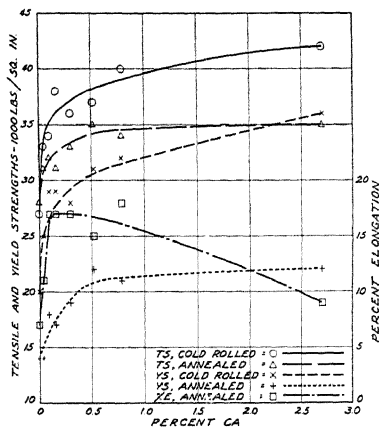


FIG. 1.—RESULTS ON MAGNESIUM-CALCIUM ALLOYS.

in strength is most rapid up to 0.3 per cent.

Magnesium-cerium Alloys.—The results for the magnesium-cerium alloys are embodied in Fig. 2. We see that cerium behaves much like calcium. There is a rapid rise in ductility up to about 0.1 per cent, after which it slowly decreases. The yield strength in the annealed condition continues to increase out to the limit of composition studied. The rise in strength is most rapid up to 0.1 per cent. The properties of the cold-rolled metal above 0.5 per cent could not be obtained, because the hot-rolled strip was too hard to withstand further cold-rolling. These alloys were made by adding 98 to 99 per cent pure cerium, free from other rare earths; not the "Mischmetal" containing 50 per cent Ce, which often is referred to as "cerium."

Magnesium-gallium Alloys.—Fig. 3 shows how the expensive metal gallium increases the ductility of magnesium. Because of the nature of the constitutional diagram, and the similarity of gallium to aluminum, it is probable that the ductility would eventually decrease, as the percentage of gallium increased.

These alloys were made with sublimed magnesium, which accounts for the lower strength at 0 per cent Ga in Fig. 3, as compared to Figs. 1 and 2. The rate of

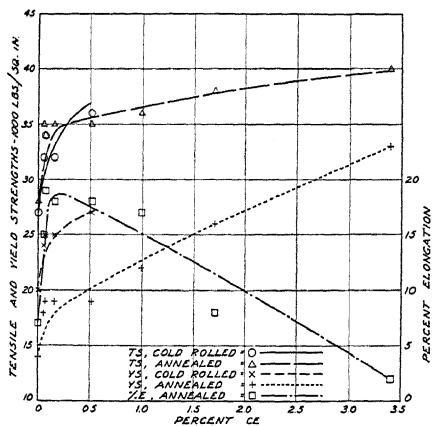


FIG. 2.—RESULTS ON MAGNESIUM-CERIUM ALLOYS.

increase of strength is most rapid up to 0.1 per cent Ga.

Magnesium-thorium Alloys.—The effect of thorium is shown in Fig. 4. The base magnesium had been sublimed. There is as yet some uncertainty as to the precise rate of rise of the elongation in the annealed state, which will require further work to eliminate. The existence of ductile alloys at 2 to 3 per cent Th is a positive finding, however. Age-hardening is observed at 2 per cent and above.

DISCUSSION OF RESULTS

Table 1 summarizes the properties of the best alloys of each system, within the limits studied, considered from the standpoint of ductility.

These metals belong to the group of alloying elements that increase the ductility of magnesium. The magnitude of the increase in ductility is such as to put them into a class with zinc, silver, aluminum, cadmium and thallium.¹

The constitutional diagram of all the binary systems reported on to date is known, except for thorium.^{2,3} A study of these diagrams leads one to the conclusion

that the maximum of ductility exists at a composition where the added element is largely in solid solution. Presence of a second phase decreases the ductility. The

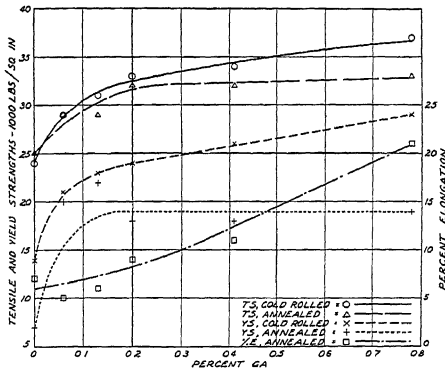


FIG. 3.—RESULTS ON MAGNESIUM-GALLIUM ALLOYS.

converse of this first proposition is not true; the existence of a range of solid solubility does not guarantee the production of an increase in ductility (tin, lead, bismuth). Since thorium does produce an increase in

TABLE 1.—*Properties of Alloys of Highest Ductility*

| Composition, Per Cent | Elonga- tion, Per Cent | Yield Strength, 1000 Lb. per Sq. In. | | Tensile Strength, 1000 Lb. per Sq. In. | |
|--------------------------|------------------------------|--|-----------------|--|-----------------|
| | Annealed | Annealed | Cold- rolled | Annealed | Cold- rolled |
| 0.3 Ca.... | 17 | 20 | 29 | 33 | 37 |
| 0.2 Ce.... | 19 | 18 | 25 | 34 | 34 |
| 0.8 Ga ^a ... | 21 | 19 | 29 | 33 | 37 |
| 2.0 Th.... | 22 | 18 | 26 | 33 | 32 |

^a Sublimed Mg base.

ductility, and also causes age-hardening, it is probable that there is a considerable range of solid solubility in the magnesium-thorium system. It has been observed also that in systems where the range of solid solubility is very small, there is little or no increase in ductility (copper, nickel, antimony). This is in agreement with the previous statement about the effect of the presence of a second phase.

The ductility of single crystals of magnesium, magnesium plus aluminum and magnesium plus zinc has been studied.² Both aluminum and zinc cause the ductility

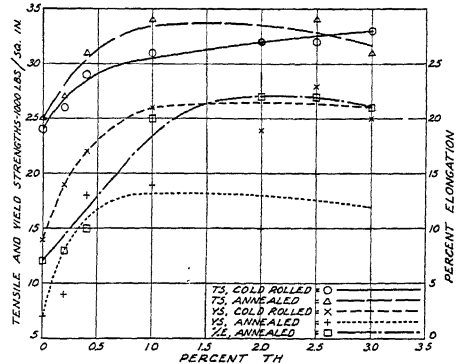


FIG. 4.—RESULTS ON MAGNESIUM-THORIUM ALLOYS.

of a single crystal to decrease. The increase in ductility of the polycrystalline metal may be due to modes of deformation that are not observed in single crystals. Certainly the crystallites are subjected to a much more complicated system of stress than can be enforced on a single crystal. It is probable that the other ductility-producing elements act in the same way. In both single and poly-crystals, foreign atoms increase the strength.

CONCLUSION

Calcium, cerium, gallium, and thorium increase the ductility of magnesium markedly, and also increase its strength. In this respect they are similar to zinc, silver, aluminum, thallium, and cadmium. They are much different from antimony, bismuth, copper, lead, nickel, and tin, which have little or no beneficial effect on ductility.

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2. A. Beck: *Magnesium und Seine Legierungen*. Berlin, 1939. J. Springer.
3. J. L. Haughton and W. E. Prytherch: *Magnesium and Its Alloys*. London, 1937. His Majesty's Stationery Office.

DISCUSSION

(*L. W. Eastwood presiding*)

G. EDMUNDS,* Palmerton, Pa.—The effects upon ductility of either aluminum or zinc present in solid solution in magnesium are given as an increase of ductility for rolled, annealed specimens, but a decrease of ductility for single crystals. This difference might well be the result of a change of mode of deformation, as suggested by Mr. McDonald. One can ask what is meant here by the expression “mode of deformation.” In a broad sense it is inclusive. Deformation can occur as a displacement of grains as a whole with a minimum of grain distortion, or primarily as grain distortion with a minimum of relative grain displacement. In the first case, a relatively brittle single crystal and a ductile polycrystalline sample of the same alloy would be consistent, and strengthening, as by alloyage, of the grain could contribute to increased ductility.

Should the deformation consist primarily of grain distortion, the complex stress system set up in polycrystalline aggregates may become especially important. Then, however, in randomly oriented specimens there would be present crystallites most unfavorably oriented for deformation and miniature fractures would be anticipated unless the stress requirement for fracture exceeded that which could be imposed by neighboring crystallites more favorably oriented for deformation. If, on the latter account, fractures were hindered or precluded, the aggregate might exhibit good ductility while a single crystal of unfavorable orientation might be brittle. Grain refinement, as by an alloying addition, even though it tended to embrittle single crystals, might then toughen rolled, annealed aggregates. On the other hand, if the miniature fractures should develop and propagate, owing to stress concentrations caused by them, the polycrystalline material might be nearly as brittle as would single

crystals that were oriented unfavorably for deformation.

Grain orientation may also be significant in itself, and since rolled specimens even after annealing commonly exhibit a special orientation texture, which may be either favorable or unfavorable for a particular deformation, ductility may be obtained with such specimens even though single crystals deformed in some ways may be brittle. Alloying, by altering high-temperature modes of deformation, may result in a different orientation texture.

It has not been intended here to give a complete analysis of the possible ways of rationalizing an embrittlement by alloying of a single crystal with a toughening by the same alloying of rolled or rolled and annealed specimens. Obviously many other factors, such as grain shape, strain-hardening, mechanisms of slip and twinning, and dendritic structures could be brought into the discussion. Various considerations that have been given seem to suffice to show, however, that it does not seem strange that there may exist a reversal in effects of alloying upon the ductility of single crystals and polycrystalline aggregates.

J. C. McDONALD (author's reply).—Mr. Edmunds' remarks throw considerable light on the experimental findings. By “modes of deformation” is meant the different ways in which a single crystal can change its shape, under stress, without fracturing; i.e., slip or twinning on a certain plane, or planes. Only a few such mechanisms have been observed in isolated single crystals of magnesium and a few of its alloys. In polycrystalline material, the interaction of the crystals may bring other mechanisms into play. As Mr. Edmunds points out, these new mechanisms may be different for alloys than for the pure metal. This would create a difference in the preferred orientation of the rolled metal, in the first place, and, in the second place, would cause it to deform differently when tested.

* Research Division, The New Jersey Zinc Co.

Grain Orientation of Cast Polycrystalline Zinc, Cadmium and Magnesium

BY GERALD EDMUNDS,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1940)

CASTINGS of pure metals and many alloys usually have a coarse-grained structure characterized by long columnar grains throughout the main body of the casting. Frequently, the surface exhibits finer, sometimes nearly equiaxed grains, and such grains may also compose other parts of the casting. This paper deals primarily with determinations of the grain-orientation textures of the columnar and surface grains of polycrystalline zinc castings. It includes some results upon a cadmium casting and a magnesium casting. A hypothesis is developed to account for the observations on columnar grains and to use as a basis for predicting orientations in other cast metals.

A general description of the position of the columnar grains in castings is that their long axes are approximately parallel to the direction of the thermal gradient during crystallization. Thus, in cylindrical castings the columnar grain axes tend to be radial, and in large flat castings where most of the cooling is through one or both of the large mold surfaces they tend to be perpendicular to the mold surfaces. At the edges and corners the direction of heat flow and therefore the position of the grains is more complex. Actually observation shows that even in castings made in flat molds the cooling seems to be somewhat irregular, since columnar grains tend to emanate from certain areas of the cooling surface, indicating that thermal contact was better there than in neighboring areas.

The nucleus from which a columnar grain grows may be so oriented that its direction of maximum growth rate does not coincide with the direction of the thermal gradient. In this case the long axis of the grain probably assumes an intermediate position.

Notwithstanding these minor irregularities, the situation does exist that the long axes of the columnar grains are generally disposed approximately perpendicular to the mold surface.

Schmid and Wasserman¹ and Nix and Schmid² have determined the orientation texture of columnar grains in castings of several cubic, tetragonal, hexagonal close-packed and rhombohedral metals. For zinc and cadmium, they report the basal plane to be parallel to the columnar grain axes, with no preference for any particular direction in this plane to coincide with the grain axes. This texture, termed a ring fiber texture,³ is uncommon in metals; zinc and cadmium are the only ones reported to exhibit it. Generally, it is stated, a simpler texture exists in which a principal, though not necessarily the most closely packed, crystallographic direction is parallel to the direction of heat flow. In cast magnesium (also hexagonal close packed) they report a digonal axis I, $[100]$ direction, parallel to the direction of heat flow. The writer is not aware of any other orientation-texture determinations on cast polycrystalline hexagonal metals.

In view of the observations reported in the present paper it is of interest also to note that Nix and Schmid stated that a

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* Investigator, Research Division, The New Jersey Zinc Co. (of Pa.), Palmerton, Pa.

¹ References are at the end of the paper.

departure from randomness of orientation is especially to be expected in the columnar grains; they do not seem to have determined the orientation texture at the surface

tion adopted for most of the specimens consisted in sawing with a power saw to within about $\frac{1}{8}$ in. of the surface to be examined, then milling with a cut of about $\frac{1}{16}$ in.

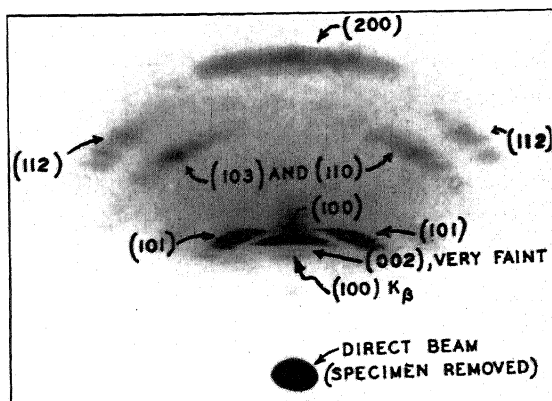


FIG. 1.—TYPICAL DIFFRACTION PATTERN OBTAINED FROM COARSE-GRAINED ZINC SPECIMEN (FIG. 7) USING ROTATING-TRANSLATING SPECIMEN X-RAY SURFACE-REFLECTION METHOD OF ORIENTATION-TEXTURE DETERMINATION. IMPORTANT REFLECTIONS ARE INDEXED ON FIGURE.

of castings. Desch⁴ states that surface chill crystals appear to be randomly oriented.

EXPERIMENTAL PROCEDURE

Thirty-six zinc castings were prepared and their orientation textures determined at various levels. The castings were made in a variety of sizes, using cast iron, steel, and graphite molds and a wide range of metal and mold temperatures and other conditions. Only a few representative ones will be described. One casting each of cadmium and magnesium was studied.

*Methods Used for Orientation Determinations**

Orientation textures were determined at the original surfaces and at various levels in the castings on surfaces parallel to the cooling surface. The internal surfaces required great care in preparation to avoid mechanical twinning, which would lead to erroneous results. The method of prepara-

tion followed by successively lighter cuts until the last, about 0.002 to 0.005 in., brought the specimen to about $\frac{1}{64}$ in. from the final surface. The remaining metal was removed by metallographic polishing and deep etching, usually with a solution of 20 grams CrO_3 , 1.5 grams Na_2SO_4 and 100 c.c. water.

Several methods of determining orientations were used; the most significant and the only ones reported here were by X-ray diffraction. The principal method was of the surface-reflection type, using a technique that has been designated as the rotating-translating specimen X-ray surface-reflection method. The specimen is rotated about the fiber axis, in this case the direction perpendicular to the flat mold surface, and simultaneously moved side to side and back and forth in the plane of the specimen surface with the collimated X-ray beam always incident at the same angle to the specimen surface. The diffraction pattern is recorded by a photographic film beyond the specimen and perpendicular to the incident beam. For these tests Mo K_α radiation incident upon the surface at about 8° , and a specimen to film distance of

* See Indexing of Crystallographic Features, page 185.

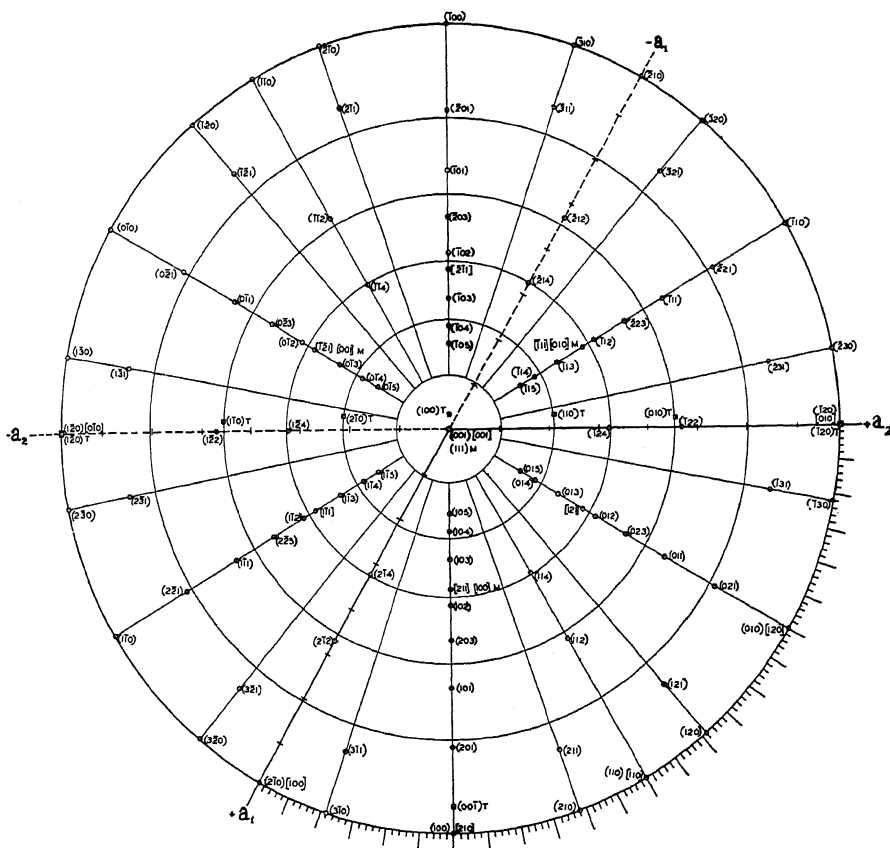


FIG. A.—STEREOGRAPHIC PROJECTION OF THE ZINC CRYSTAL (AXIAL RATIO 1.8563 AT 27°C .). Showing the crystal planes (hkl) of high atomic density, certain important directions $[hkl]$, the basal and prism planes $(hkl)T$ of one twin of the first generation, all referred to two equal horizontal axes, a_1 and a_2 , intersecting at an angle of 120° , and a third, vertical axis, c , at right angles to them, and the positions of the Miller hexagonal-rhombohedral axes with their Miller indices $[hkl]M$.

Indexing of Crystallographic Features: The three-index system has been used throughout. This is based upon two equal axes, a_1 and a_2 , along close-packed directions and intersecting at an angle of 120° and a third axis c normal to the plane of the other two. A stereographic projection of the zinc crystal is given here (Fig. A). The projections of other hexagonal closepacked metals are similar, differing only in the angle between the hexagonal axis and the pyramidal planes (because the axial ratio (c/a) differs).

The four-index system (Miller-Bravais) indices for planes are obtained by supplying between the second and third index an additional one equal to the sum of the first two with the sign reversed, thus:

$$(2\bar{1}0) \text{ in the three-index system} \equiv (2\bar{1}\bar{1}0) \text{ in the Miller-Bravais system.}$$

Transformations of indices of crystallographic directions are *not* made in this way. (Line indices are the coordinate differences between adjacent atom positions along the crystallographic line (or direction).) In contrast to the isometric system (cubic crystals), crystallographic directions normal to crystallographic planes do not in general bear the same indices as the planes. The normals to pyramidal planes have no crystallographic significance.

7 cm. have been used. The area of specimen surface examined was about one square inch. With this method, every grain extending to the surface yields diffraction effects

rotated about its axis and moved back and forth in the direction of the axis.

Back-reflection Laue X-ray patterns were prepared from 20 grains of one speci-

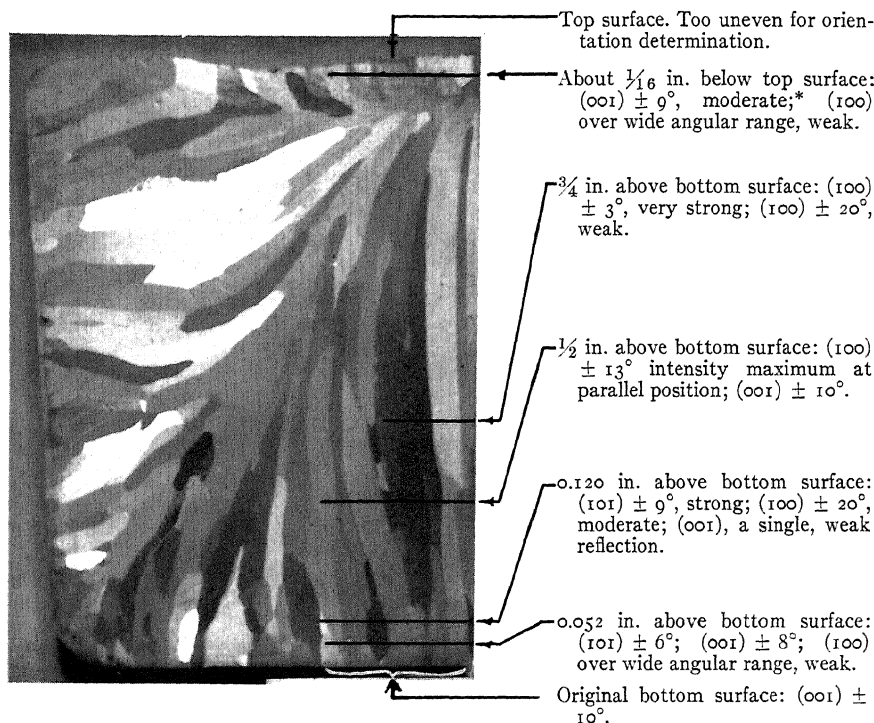


FIG. 2.—CASTING NO. 1. HALF OF VERTICAL CROSS SECTION.

Etch: concentrated HCl. Original magnification 2; reduced $\frac{1}{7}$ in reproduction.

The orientations* at various levels as indicated are given at the right; no determinations were made beyond the ends of the ruled lines. The ruled lines are the traces of the planes of polish upon which orientations were determined.

* Where orientations are expressed, for example, as: “(001) $\pm 9^\circ$, moderate,” this is to be read as: “The (001) planes have a mean position parallel to the plane of polish, the angular variation from this position is 9° .” The plane of polish upon which the orientation is determined is perpendicular to the average direction of heat flow; correspondingly, it is approximately perpendicular to the axes of the columnar grains. The more predominant orientations are given first. This means of expressing orientation textures has been used throughout.

at some time during the exposure, so that even coarse-grained specimens yield a pattern that is readily interpreted. Fig. 1 is a typical diffraction pattern. The validity of this method was established by comparison of results with those obtained on individual grains by the back-reflection X-ray method.

For cylindrical specimens having radial grains the X-ray beam is incident tangentially on the specimen. The specimen is

men from casting No. 2 (zinc) and 10 grains of casting No. 7 (magnesium). The individual grains of the stationary specimen were irradiated with a collimated beam of unfiltered copper X-rays (50 kv. P) incident upon the specimen normal to the cooling surface. The pattern was recorded on a flat photographic film at a distance of 3 cm. The orientation was determined by measurements on stereographic projections.

DESCRIPTION OF SPECIMENS AND
RESULTS OBTAINED

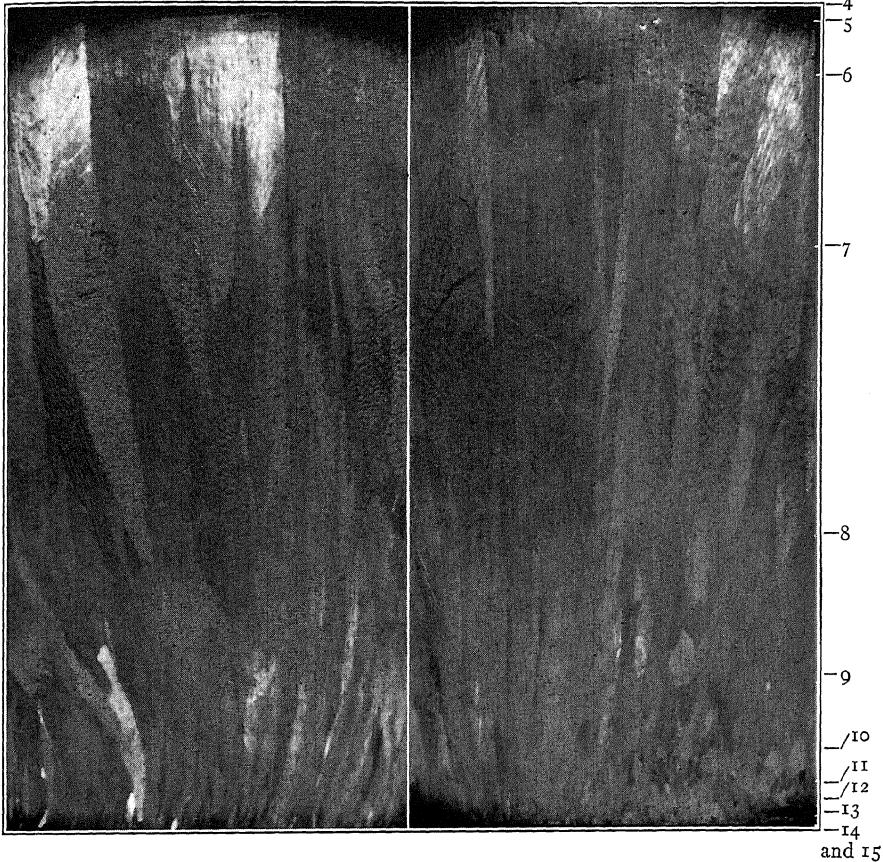
Casting No. 1.—Special High Grade zinc*
was poured into a heavy, open-top cast-iron

B

Orientations at various levels are given
beside a macrograph of a typical cross section
in Fig. 2.

Casting No. 2.—High Grade zinc was
poured $2\frac{7}{8}$ in. deep into a large cast-iron

A



and 15

FIG. 3.—VERTICAL SECTIONS, $1\frac{1}{2}$ INCHES WIDE, THROUGH $2\frac{7}{8}$ -INCH DEEP CASTING NO. 2, SHOWING TWO SIDES OF SPECIMEN LATER CUT FOR EXAMINATIONS OF HORIZONTAL SECTIONS.

Numbers at right indicate levels at which macrostructures and orientation textures (Figs. 4 to 15) were determined, and correspond to those figure numbers. Letters A and B above the macrographs are used to show the correspondence of sides as designated in the captions to Figs. 4 to 15. Etch: Concentrated HCl.

Original magnification 1.8; reduced $\frac{1}{4}$ in reproduction.

mold (about 40 in. long by 3 in. wide by 2 in. deep). Cooling proceeded chiefly from the mold, and partly from the exposed top surface.

tray. Cooling from the top surface was prevented by using a heater above the casting so that the cooling was from the bottom.

One specimen, $1\frac{1}{2}$ in. square by $2\frac{7}{8}$ in. high, was cut far enough from any edge of the casting to avoid edge cooling effects.

* Grades of zinc used are designated according to the Standard Specification for Slab Zinc (Spelter); A.S.T.M. designation, B6-37.

The macrostructure of vertical and horizontal sections of the casting and the orientation-texture data are shown in Figs. 3 to 15.

The orientations of 20 individual grains,

and that freezing from the top was not prevented but was accentuated by blowing cold air over the surface.

A specimen, 2 in. square by $1\frac{7}{16}$ in. high, was cut from near the center. The macro-

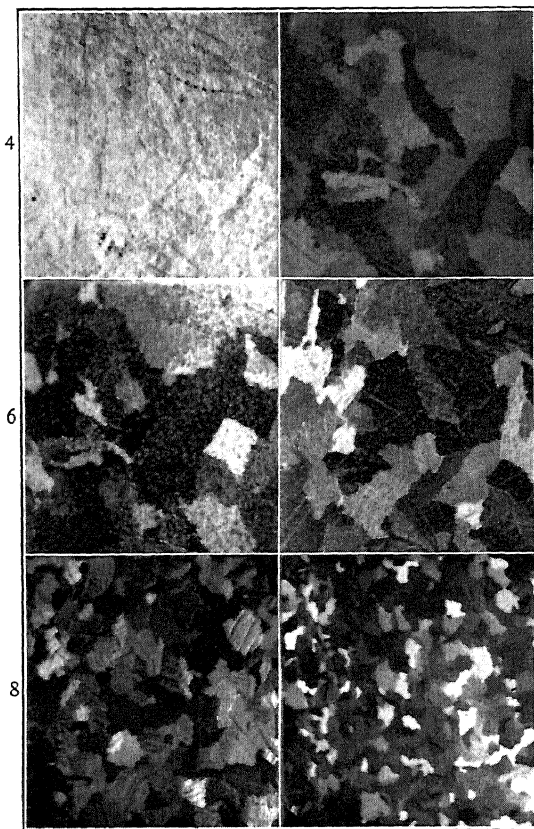


Fig. 4: original top surface: $(100) \pm 8^\circ$, strong; $(001) \pm 8^\circ$, weak.

Fig. 5: $\frac{1}{16}$ in. below top surface: $(100) \pm 9^\circ$.

Fig. 6: $\frac{1}{4}$ in. below top surface: $(100) \pm 12^\circ$.

Fig. 7: 2 in. above bottom surface: $(100) \pm 13^\circ$.

Fig. 8: 1 in. above bottom surface: $(100) \pm 15^\circ$, very strong; $(001) \pm 10^\circ$, weak.*

Fig. 9: $\frac{1}{2}$ in. above bottom surface: $(100) \pm 19^\circ$, strong; $(001) \pm 19^\circ$, moderate.*

FIGS. 4 TO 9.—HORIZONTAL SECTIONS THROUGH $2\frac{7}{8}$ -INCH DEEP CASTING NO. 2.

Etch, except Figs. 4 and 15, which were not etched: concentrated HCl. $\times 1.8$.

Only about a quarter of each surface is shown; the top edge is adjacent to side A and the left edge to side B of Fig. 3.

Orientation textures are given at the right. The means used in describing orientations is given in the explanatory note under Fig. 2.

* The (001) plane reflections probably derived from mechanical twins produced during preparation of the specimen. Other determinations (Figs. 5 and 7) likewise yielded these originally, but after careful repolishing and etching, which removed many of the surface twins, no (001) plane reflections were obtained.

† A poorly defined pattern.

Fig. 16, at the level of Fig. 7, 2 in. above the bottom surface, were also determined by the back-reflection Laue method and are shown stereographically in Fig. 17.

Casting No. 3.—Casting No. 3 was like No. 2 except that it was only $1\frac{7}{16}$ in. thick

structure on a vertical section and the orientation texture determined on horizontal sections at four levels are given by Fig. 18.

Casting No. 4.—High Grade zinc was poured into a 9-in. long by 2-in. wide by

7-in. deep mold. One end of the mold was of water-cooled steel, and the other end, sides and bottom were (preheated) Transite, and the top was open.

Specimens were cut through the grains

diameter vent-end grip section of this bar. A section through the bar and the orientation data for various levels in it are shown in Fig. 20. The removal of metal to the levels examined was entirely by etching.

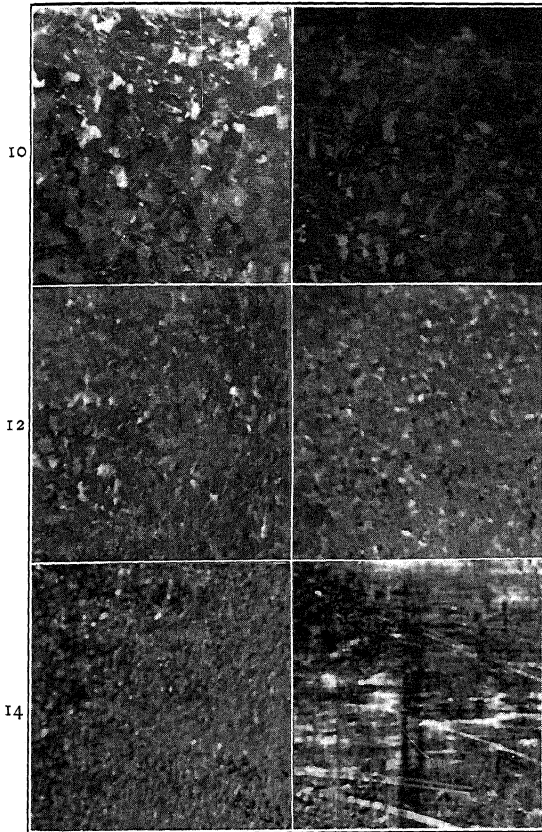


Fig. 10: $\frac{1}{4}$ in. above bottom surface: $(100) \pm 14^\circ$.

Fig. 11: $\frac{5}{32}$ in. above bottom surface: $(100) \pm 29^\circ$.

Fig. 12: $\frac{1}{16}$ in. above bottom surface: (100) over a wide angular range; \dagger (001) over a wide angular range. \dagger

Fig. 13: $\frac{1}{32}$ in. above bottom surface: $(001) \pm 4^\circ$, moderately strong; $(100) \pm 31^\circ$, moderate.

Fig. 14: bottom surface: $(001) \pm 9^\circ$, very strong; (100) , extremely weak.

Fig. 15: original bottom surface: $(001) \pm 7^\circ$, very strong; (100) , extremely weak.

FIGS. 10 TO 15.—CAPTION AND NOTES UNDER FIGS. 4 TO 9.

grown from both the steel end plate and one of the Transite sides.

A horizontal section through the entire casting is shown in Fig. 19. Orientation textures were determined on vertical sections as indicated.

Casting No. 5.—Special High Grade zinc was cold-chamber die-cast in the form of a standard* $\frac{1}{4}$ -in. diameter round tensile bar. A specimen was cut from the $\frac{3}{8}$ -in.

Casting No. 6.—Cadmium (99.9+ per cent Cd grade) was cast about $1\frac{1}{2}$ in. deep in a 4-in. square Transite-sided mold having a 2-in. thick steel bottom. A specimen, $1\frac{1}{2}$ in. square by 1.1 in. high, was cut from the center of the casting.

The macrostructures of a horizontal section, 1.1 in. from the bottom of the casting, and a vertical section showing the structure from the bottom upward for 1.1 in., together with orientation data, are given in Fig. 21.

* Tentative Specifications for Zinc-base Alloy Die Castings, A.S.T.M. Designation, B86-38T.

Casting No. 7.—Magnesium* cast about 6-in. diameter by 20 in. high with cooling entirely from the bottom. The (horizontal) section used was cut about 15 in. from the

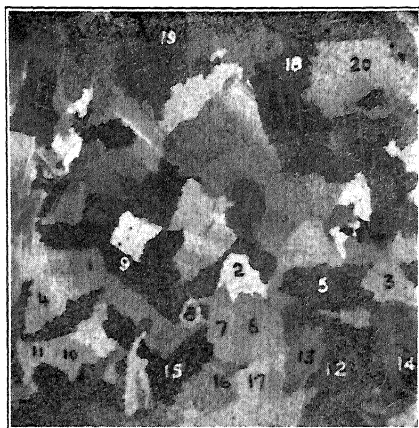


FIG. 16.—HORIZONTAL SECTION THROUGH $2\frac{7}{8}$ -INCH DEEP CASTING NO. 2, 2 INCHES ABOVE BOTTOM SURFACE.

Etch: concentrate HCl. Numbers designate grains whose individual orientations are given by Fig. 17. Original magnification about 1.8; reduced $\frac{1}{4}$ in reproduction.

bottom of the casting. The surface was prepared by lathe turning followed by deep etching. Because of the large grain size the only orientation determination on this casting was by the back-reflection Laue technique. The orientation of 10 grains was determined, as indicated by Figs. 22 and 23.

Results

These results are summarized and compared with those of Schmid and Wasserman¹ and Nix and Schmid² in Table 1.

There is a difference between the present results on zinc and cadmium and those of the earlier investigators in that they did not observe the preference for a definite growth direction, presumably because too few (from 6 to 10, according to their report) crystals participated in producing the patterns. Orientation textures at and near the surface were not determined.

* Furnished by the Dow Chemical Co. through the courtesy of Dr. J. D. Hanawalt.

The difference between the results on magnesium cannot be accounted for so simply. Possibly the texture of magnesium varies with the casting conditions; e.g., the

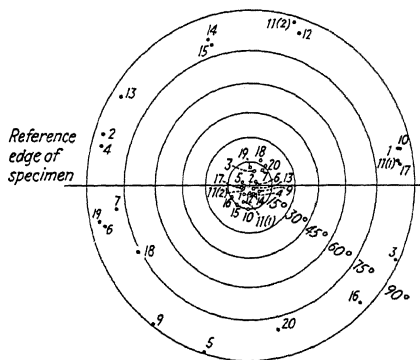


FIG. 17.—STEREOGRAPHIC PROJECTION OF ORIENTATIONS OF INDIVIDUAL GRAINS DESIGNATED BY CORRESPONDING NUMBERS IN FIG. 16.

Poles of (100) planes are shown by open circles, poles of (001) planes by filled circles. Specimen surface is parallel to original surface of casting and is the plane of projection.

rate of cooling. Scheil⁵ reported such a difference for salts in discussing Nix and Schmid's paper. In the sample used here the rate of freezing must have been very

TABLE 1.—Orientation Textures in Cast Polycrystalline Zinc, Cadmium and Magnesium

| Metal | Part of Casting | Plane Parallel to Cooling Surface | |
|------------|--------------------|-----------------------------------|--|
| | | Present Determination | Reported by Schmid and Wasserman and Nix and Schmid ^a |
| Zinc..... | Chilled surface | (001) | Not stated |
| | Columnar grains | (100) ^b | (001) perpendicular |
| Cadmium.. | Intermediate | (101) ^c | None stated |
| | Air cooled surface | (001) | Not stated |
| Cadmium.. | Chilled surface | (001) | Not stated |
| | Columnar grains | (100) ^b | (001) perpendicular |
| Magnesium. | Columnar grains | (205) ^b | (110) ^d |
| | | (100) | |

^a The indices have been changed to conform to the system used here.

^b Approximately, see later discussion.

^c Not always found. Where it has been observed it has been mixed with orientations described above or randomly oriented grains.

^d The text and table in Nix and Schmid's paper do not agree; their table gives this as (100).

slow; no experiments were conducted to investigate effects of other cooling rates. The orientation texture of magnesium is discussed further in the next section.

dodecahedron are also along the cube axes, and completely analogous results follow, again demonstrated by experiment.^{1,2}

Crystals of lower symmetry cannot be

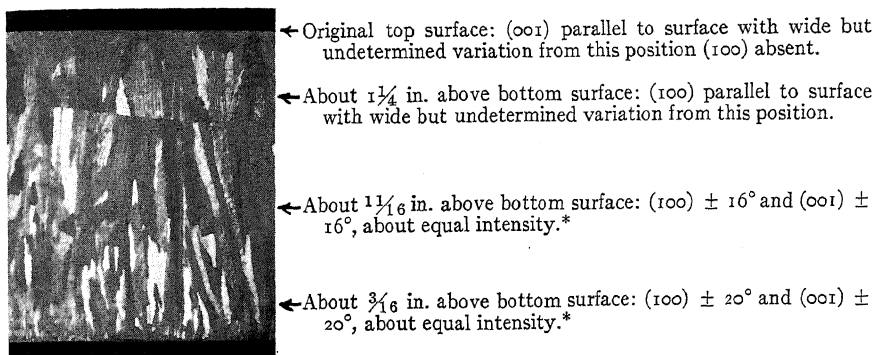


FIG. 18.—VERTICAL SECTION THROUGH $1\frac{9}{16}$ -INCH DEEP CASTING NO. 3.

Etch: concentrated HCl. About natural size. Orientations at various levels are indicated at right.

* This surface contained many twins, presumably developed during its preparation. The (001) reflections may have been due to them. See also explanatory note under Figs. 4 to 15.

RATIONALIZATION OF THE ORIENTATION TEXTURES OF CAST METALS

A. Bravais⁶ has concluded that the faces most likely to bound a natural crystal are, in general, those of greater reticular (atomic) density. C. H. Desch⁷ stated, on this basis, that "The more open the packing of a plane . . . the greater its velocity of growth in a direction normal to itself, and the less its chance of survival during continued growth."

The application of this rule to the cubic metals is simple. In face-centered cubic metals the octahedral {111} planes are those of closest packing. The longest dimensions through an octahedron are along the directions of the cube axes, and hence by the Bravais rule the maximum growth rate would be along the [100] directions. The columnar grain axes of face-centered cubic metals have been found^{1,2} to be approximately parallel to [100] directions, in agreement with the rule. In body-centered cubic metals the {110} planes are those of closest packing. The longest dimensions through a

treated so simply. In the hexagonal close-packed metals, such, for example, as zinc, cadmium and magnesium, the planes of closest packing are the basal (001) planes, and these alone cannot completely bound a crystal. The next most closely packed planes are the second-order prism {110} planes. Based on consideration of these two types of planes alone, the Bravais rule, with some extension, would indicate that a hexagonal prism bounded by (001) and {110} planes would be the natural form; the ratio of the height to the thickness of the natural crystal would depend upon the relative atomic density on these two types of planes, the crystal being lower the greater the density on (001) planes relative to {110} planes. Since the ratio of these atomic densities is directly proportional to the axial ratio (c/a) of the crystallographic axes, the natural form of a crystal of large axial ratio would tend to be squatty, and one of small axial ratio tall. The six equal and longest dimensions, corresponding to the directions of maximum growth rate, through such a prism would be directions

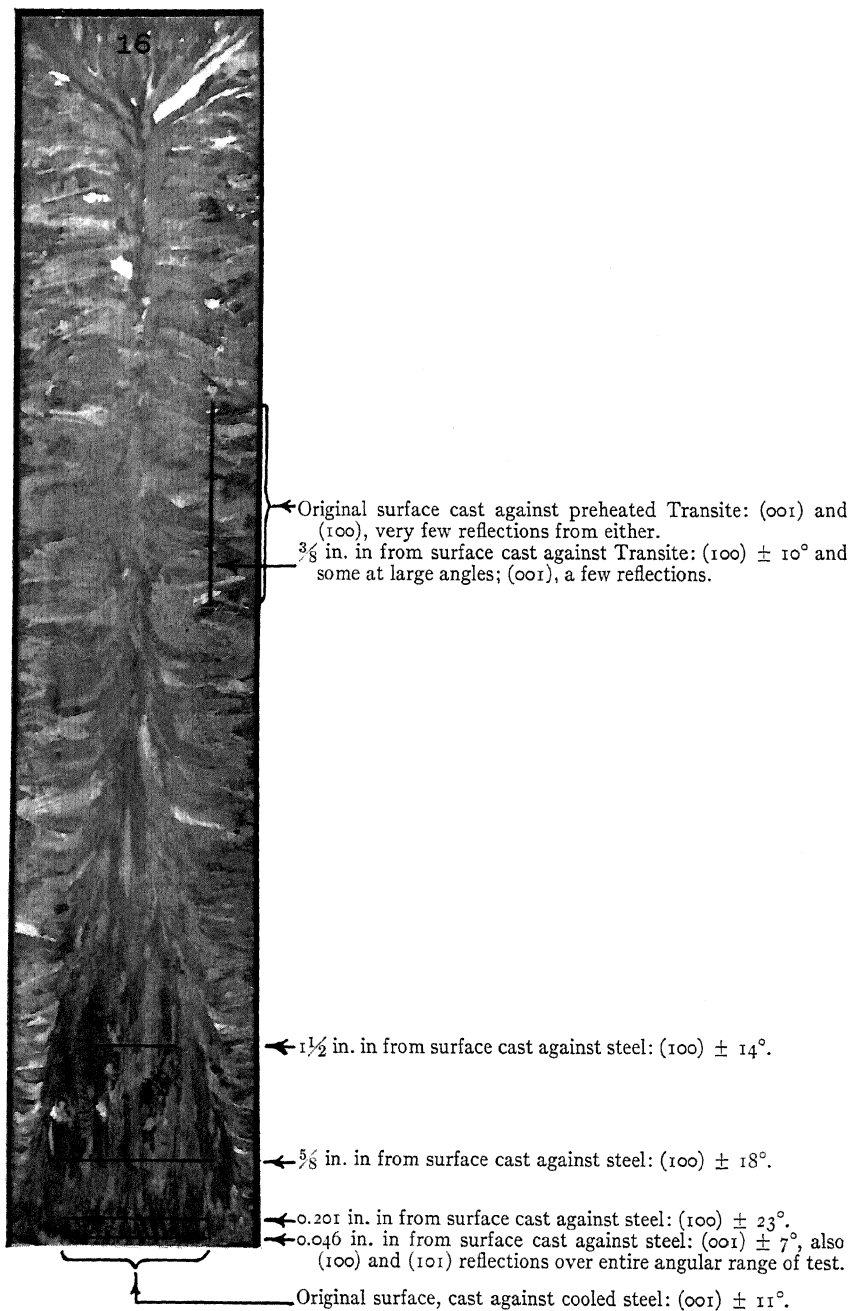


FIG. 19.—HORIZONTAL SECTION THROUGH CASTING NO. 4.
Etch: concentrated HCl. About 0.7 \times . Orientations as determined on the indicated vertical sections are given at the right.

parallel to $\{110\}$ planes, and, qualitatively, the angle between the hexagonal axis $[001]$ and the direction of maximum growth rate would increase with an increase in the axial

principal crystallographic direction or perpendicular to a principal crystallographic plane.

Since the ratio of atomic density of (001)

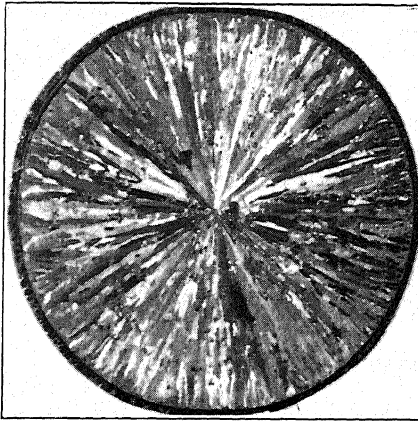


FIG. 20.—SECTION THROUGH CASTING No. 5. Etch: concentrated HCl. $\times 6$. The dark, rough rim is copper electroplate, applied to specimen to prevent loss of edge detail in polishing. Orientation textures at various levels are:

| DEPTH BELOW SURFACE, IN. | ORIENTATION | TEXTURE |
|--------------------------|-------------|--|
| Original surface.... | (001) | tangent to surface $\pm 15^\circ$ to axis of bar |
| 0.009..... | (100) | tangent to surface $\pm 25^\circ$ to axis of bar |
| 0.019..... | (100) | tangent to surface $\pm 29^\circ$ to axis of bar |
| $\frac{1}{8}$ | (100) | tangent to surface $\pm 17^\circ$ to axis of bar |

ratio (c/a). It would seem merely to be coincidence if the direction of maximum growth rate happened to be either parallel to a

TABLE 2.—*Experimental Relationships*

| Metal | Plane Approximately Normal to Columnar Grain Axis | Approximate Angle of Growth Direction to $[001]$ | Axial Ratio (c/a) |
|--------------|---|--|--|
| Cadmium.... | (100) | 90° | 1.89 at 300°C . |
| Zinc..... | (100) ^a | 90° ^a | 1.886 at 400°C . |
| Magnesium... | (205) | 34° | 1.623 at 25°C . ^c |

^a None of the 20 grains whose orientation was determined individually (Fig. 17) had its plane inclined at less than 3° , and only two had it inclined at less than 5° to the specimen surface. The number of determinations was too small to allow any particular significance to be attached to this observation.

^b $(001) \wedge \{205\} = 36^\circ 52'$.

^c Axial ratio is changed but little with temperature, at least up to 200°C . (ref. 8).



FIG. 21.—A HORIZONTAL SECTION (UPPER PHOTOGRAPH), 1.1 INCH ABOVE THE BOTTOM SURFACE, AND A VERTICAL (LOWER PHOTOGRAPH) SECTION OF CADMIUM CASTING No. 6.

Etch: concentrated HCl. Original magnification 2; reduced approximately $\frac{1}{3}$ in reproduction.

Level *a*, 1.1 in. above bottom surface $(100) \pm 22^\circ$.

Level *b*, original bottom surface $(001) \pm 17^\circ$, strong; also random orientations.

At the original top surface (not shown here) the (100) planes occupied a mean position 5° from parallelism with the surface. The observed range of orientations was $\pm 5^\circ$ from this position so that the X-ray pattern showed two diffraction arcs from (100) that touched at the middle of the pattern.

to $\{110\}$ is lower in magnesium than in zinc and cadmium, the above hypothesis led to the prediction, later confirmed by the determination reported on page 190, that the axis of the columnar grains of magne-

sium would be parallel to a $\{110\}$ plane and at an angle to the hexagonal axis smaller than the same angle for zinc. The experimental relationships are shown in Table 2.

about 1.6; according to the Bravais rule, as here extended, the orientation of columnar grains in castings of them is probably more like that of magnesium than of zinc and

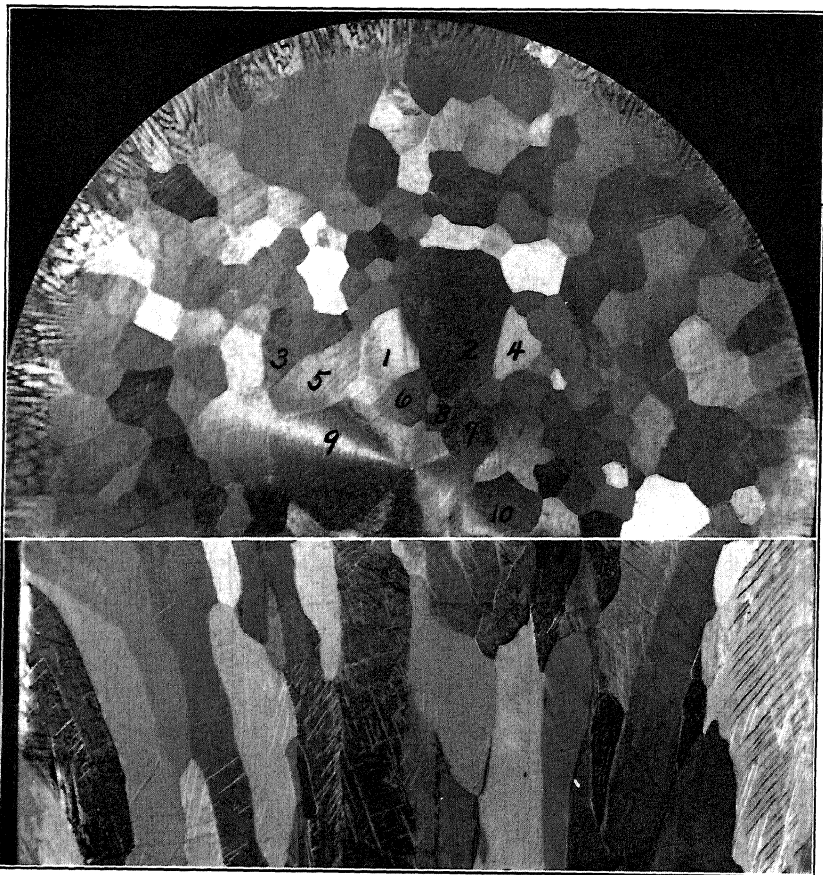


FIG. 22.—HORIZONTAL (UPPER) AND VERTICAL (LOWER) SECTIONS OF MAGNESIUM CASTING NO. 7. Etch: horizontal section, 1:2 acetic acid and H_2O ; vertical section, 10 per cent ammonium persulphate in H_2O . Slightly reduced from natural size. Numbers designate grains whose individual orientations are given by Fig. 23.

No consideration has been given in the analysis to the effect of planes of slightly lesser atomic density. The only effect that would be anticipated from including them would be to further diminish the predicted angle between the hexagonal axis $[001]$ and the direction of growth, particularly in crystals of low axial ratio.

Hexagonal close-packed metals, except zinc and cadmium, have an axial ratio of

cadmium. A similar analysis would follow directly for other crystal systems.

Attempts to rationalize the (001) surface orientation found for zinc and cadmium and the $\{101\}$ intermediate orientation found for zinc have not been successful.

CONCLUSIONS

The interior of zinc castings consists of columnar grains aligned approximately

parallel to the direction of the thermal gradient. The mean crystallographic orientation of the columnar grains is such that a $\{100\}$ prism plane is approximately perpendicular to the long axis. Whether it is precisely perpendicular to the long axis cannot be determined from the available data; the hypothesis presented suggests that it is not.

The mold surface of a zinc casting usually consists of relatively small grains with their (001) or basal planes approximately parallel to the mold surface. This is contrary to the assumptions made by other workers in this field and to the best of the writer's knowledge is the first observation of this kind on cast metals.

Intermediate between the surface and the long columnar grains frequently there is a region in which grains having a $\{101\}$ pyramid plane perpendicular to the thermal gradient predominate. Wherever observed, this orientation has always been accompanied by the orientations described above or by randomly oriented grains. Occasionally this orientation has been found at the mold surface.

In cast cadmium the surface texture and the orientation of the columnar grains are as they are in zinc. The intermediate orientation found in zinc was not looked for in cadmium.

In cast magnesium a $\{205\}$ pyramid plane is approximately perpendicular to the long axes of the columnar grains. This disagrees with results reported by Nix and Schmid.

A hypothesis is developed rationalizing the orientation texture of the columnar grains. This hypothesis led to a correct prediction of the orientation texture of magnesium. It also predicts that most hexagonal close-packed metals will have an orientation texture more like magnesium than like zinc and cadmium.

A new method of determining orientations of coarse-grained castings, designated as the rotating-translating specimen X-ray

surface-reflection method, has been employed. With its use diffraction occurs from every grain in the specimen surface, greatly facilitating fiber-axis determinations on

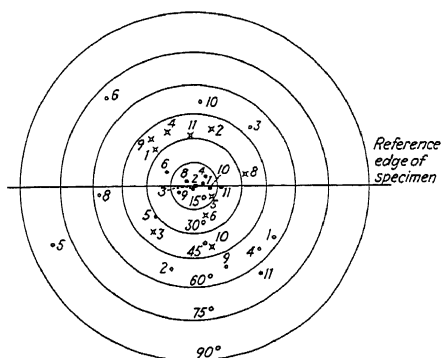


FIG. 23.—STEREOGRAPHIC PROJECTION OF ORIENTATIONS OF INDIVIDUAL MAGNESIUM GRAINS DESIGNATED BY CORRESPONDING NUMBERS IN FIG. 22.

Poles of $\{205\}$ planes have an average position close (9°) to the plane of projection and are shown by solid circles. Poles of (001) planes are shown by crosses and of $\{100\}$ planes by open circles. The specimen surface is perpendicular to the axis of the billet and is the plane of projection.

coarse-grained specimens. The validity of the method has been confirmed by orientation determinations made by the back-reflection Laue method.

ACKNOWLEDGMENTS

The writer is indebted to his colleagues for assistance and counsel, and especially to Mr. M. L. Fuller for the X-ray examinations and to Mr. H. S. Gruber for specimen preparation; to Dr. C. H. Mathewson for having incited interest in the problem, and to The New Jersey Zinc Co. for permission to conduct the investigation and publish the results.

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DISCUSSION

(L. W. Eastwood *presiding*)

J. C. McDONALD,* Midland, Mich.—Some preliminary work has been done on magnesium, in an effort to check the author's finding. The result is concordant with his to this extent: that grains have been observed whose growth axes were not parallel to the (001) plane.

The particular casting examined by the author was freezing at a rate of about 1 in. per min. at the point examined. The grains started to grow at a lower point in the casting, where the rate was higher by an unknown amount, probably not large. The uniformity of orientation observed in the surface, and its departure from the normal type explained by the author's theory, suggest a dependence of orientation on rate of cooling. At the surface of a liquid metal, the temperature gradient becomes extremely high, probably orders of magnitude higher than the gradient present in the interior of even the rapidly cooling die casting. This effect would exist even at an air-liquid interface. Under such conditions, we may speculate that the superficial layer of grains is forced to form in an orientation different from that normally occurring at lower rates of freezing. What is the author's reaction to this suggestion?

A. B. GRENINGER,† Cambridge, Mass.—Has Mr. Edmunds made observations on the dendritic habits of the hexagonal metals he has studied? I believe that dendritic growth and preferred orientation in castings must be intimately allied and a rationalization of the latter that will be worth while cannot be made until there are available a few positive statements regarding dendritic habit. In other words, the rationalization of orientation textures of cast metals should preferably be made first with reference to dendritic growth rather than to geometry of the crystal.

One of the few statements regarding habit that mineralogists accept as reasonably accurate is: Habit is a resultant of (1) the geometry of the species, and (2) its environment during the process of crystallization. The generalization of Bravais, and its extension by Mr. Edmunds, considers only geometry; hence it

is not surprising that the application of the rule does not yield wholly satisfactory results. In natural isometric metal crystals, the cube is even more common than the octahedron, and thus, according to the author's reasoning, the direction of most rapid growth should be $\langle 111 \rangle$. Actually, in natural isometric metal crystals, both $\langle 111 \rangle$ and $\langle 100 \rangle$ are common dendrite axes, but for cubic metals and alloys prepared in the laboratory, the dendrite axes are apparently always $\langle 100 \rangle$. There is little or no published information on this point; measurements have been made at Harvard on several primary solutions of copper and of iron and no axes other than $\langle 100 \rangle$ have been found.

It is to be expected, therefore, that columnar crystals of cubic metals should be oriented with the long axes nearly parallel to $\langle 100 \rangle$, for the grain orientations that survive during growth must be those whose natural direction of maximum growth velocity coincides with the direction of the temperature gradient. I know of no published data on the dendritic habits of the hexagonal metals. Judging from Mr. Edmunds' results on orientation texture, zinc and cadmium should have $\langle 210 \rangle$ parallel to the dendrite axes and magnesium would have a considerably different dendritic habit.

C. H. MATHEWSON,* New Haven, Conn.—With reference to Dr. Greninger's remarks concerning the crystalline habit of metal crystals, it may be of interest to note that silver crystallizes from dilute solution in sodium in the form of well developed simple octahedra. Primary silver crystals obtained from a mixture containing about 75 per cent of silver bore great resemblance to specimens of native silver, occurring, according to Dana, "often in groups branching at 60° parallel to the diagonals of an octahedral face." Photographs and sketches of these silver crystals are given in my paper on sodium-silver alloys.⁹

G. EDMUNDS (author's reply).—Mr. McDonald has speculated upon the origin of the surface texture of zinc and cadmium, which was found to differ from that of the interior of the castings, and has raised the question as to whether this

* The Dow Chemical Co.

† Assistant Professor of Metallurgy, Harvard University.

* Professor of Metallurgy, Yale University.

⁹ C. H. Mathewson: *Int. Zisch. Metallographie* 1911 1, 51-63.

might be due to a tendency of a different orientation texture to develop under an extreme temperature gradient. This possibility was considered, but all experiments conducted in attempts to gain support of this idea gave negative results. It was found that the depth to which this orientation persisted did not increase under conditions of rapid cooling, as by die casting. It was also found that the surface of a casting made in an open tray and cooled in still air had this surface texture. In the latter case the metal was somewhat superheated for pouring; under such conditions there would be no instantaneous metal crystallization at the surface. It is doubted that an extreme temperature gradient existed in the surface layer of the relatively high thermal conductivity melt. It seems unlikely, therefore, that the difference between surface and interior texture can be attributed to differences in thermal gradient. Several other hypotheses have also been considered in attempts to find one that would rationalize the surface-orientation texture of zinc and cadmium, but none has been successful.

I am in complete agreement with Dr. Greninger's statement that dendritic growth and preferred orientations in castings are intimately allied; in fact, I would go further and say that both are manifestations of the same influence—that is, the tendency for crystals to grow in certain directions more than in others. The hypothesis in the paper rationalizes this tendency from purely geometrical concepts. The other important influence is the interference of growing dendrites upon one another, allowing survival only of those having

a direction of rapid growth nearly parallel to the thermal gradient.

As far as observations of dendrite habits for the hexagonal metals are concerned, these have been made on both zinc and cadmium. Rather indistinct dendrites are to be seen on Figs. 3, 16 and 18. The general pattern is of nonisomorphous impurities having been deposited in films parallel to basal planes. Unrestricted growth yields dendrites, whose trunks and branches have as their axis (at least approximately) a direction [210].

In his other comment Dr. Greninger states that "in natural isometric metal crystals, the cube is even more common than the octahedron" and that thus, according to the hypothesis in the paper the direction of most rapid growth should be [111]. This statement is contrary to that of Guillet and Portevin;¹⁰ in reporting upon the classic work of Tschernoff and of Osmond, they state that "with pure metals and solid solutions the development nearly always occurs along the axes of an octahedron* forming tree-like structures known as crystallites or dendrites . . . which, if allowed to develop freely and at the same speed in all directions, would finally take the form of an octahedron."

Dr. Greninger later goes on to say that "for cubic alloys prepared in the laboratory, the dendrite axes apparently are always [100]." This, of course, is in complete agreement with the older results referred to and the hypothesis that has been presented.

¹⁰ Guillet and Portevin: *Metallography and Macrography*, 69. London, 1922. G. Bell & Sons, Ltd.

* "Most metals crystallise in the cubic system, the directions of the dendrite branches being the quaternary axes of the cube."

Studies upon the Corrosion of Tin—Effects of Cations in Carbonate Solutions and Effects of Alloying Elements

BY GERHARD DERGE,* MEMBER A.I.M.E., AND HAROLD MARKUS*

(New York Meeting, February 1941)

THE first paper¹ of this series described a technique of careful surface preparation by means of which reproducible results may be obtained from potential measurements of the behavior of tin in carbonate solutions with a pH range from 8.4 to 11.2. It then went on to establish the behavior of pure tin electrodes under these conditions and showed that the metal remains active at all times, though the steady potential attained after several hours decreases from 1.12† volts at a pH of 12.6 to 0.6 volts at a pH of 8.4. This behavior may serve as a norm with which all other data can be compared. In the second paper,² small amounts of other anions were added to the carbonate solutions and the conclusion was reached that the common impurities encountered in alkaline materials packaged in tin do not increase corrosion. In fact, in some cases these anions may actually promote the formation of protective films.

The present paper rounds out this survey by presenting data on the influence of cations added to the carbonate solutions, as well as the effect of alloy additions to the tin. In many cases the potential data are supplemented with weight-loss measurements. Information is also presented on the

effects of some additional anions, the influence of gases above the electrolyte, the behavior of high-purity tin, and the effect of atmospheric oxidation on the corrosion resistance of the above-named alloys. Analysis of the entire body of data discloses some general rules applicable to corrosion in carbonate solutions. The experimental methods used are the same as those previously described.

EXPERIMENTAL DATA

Cations.—The carbonates of the cations K^+ , Li^+ , NH_4^+ , which are soluble, were studied in the same way as the anions, by adding 0.01 mol of the metal carbonate to one liter of 0.1 M sodium carbonate solution, pH 11.2, or to 0.1 M sodium bicarbonate, pH 8.4. The other metallic carbonates are only slightly soluble, of the order of 10^{-3} mols per liter or less, and the sodium carbonate solutions were saturated by adding excess reagent several days before the experiment, shaking frequently, and filtering just before use. The chemicals were c.p. grade in each case except the indium salt. This salt was prepared by solution of the metal in hydrochloric acid and precipitation by addition of Na_2CO_3 . These cations may be divided into two classes, according to their effect on the potential behavior of the tin: (1) normal, (2) passive.

To offer a basis of comparison, curves 1 of Figs. 1 and 2 are given to illustrate the behavior of tin in carbonate solutions saturated with $CaCO_3$. These curves are the

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† References are at the end of the paper.

‡ Throughout this series potential values are referred to a saturated calomel cell as zero, with noble metals like silver negative; i.e., increasing positive values indicate a greater tendency to corrode.

same as those obtained from solutions without Ca^{++} additions and are classed as normal. The same curves also typify the effect of additions of In^{+++} , Li^+ , Fe^{++} ,

anions that were not reported in the previous paper will be described here. Arsenate ion falls in class 1 above and in the previous paper;² i.e., it has little or no effect upon

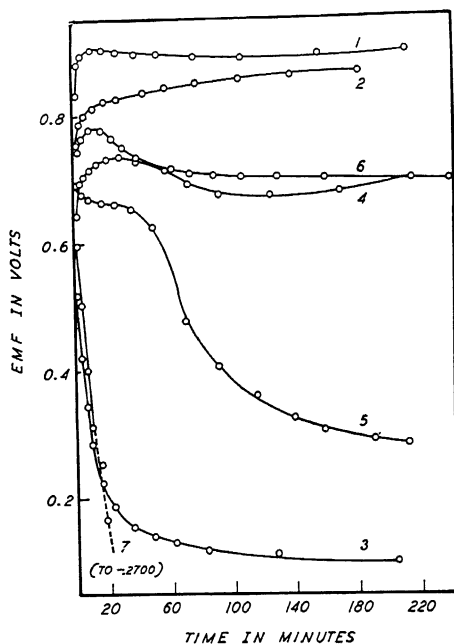


FIG. 1.—TIME-POTENTIAL CURVES SHOWING INFLUENCE OF ADDED CATIONS ON BEHAVIOR OF TIN IN CARBONATE SOLUTIONS WITH pH 11.2.

| | |
|---------------------------|---------------------------|
| Curve 1, Ca^{++} | Curve 5, Pb^{++} |
| Curve 2, Mg^{++} | Curve 6, Ni^{++} |
| Curve 3, Cu^{++} | Curve 7, Ag^+ |
| Curve 4, Zn^{++} | |

Cd^{++} , Mn^{++} , Ba^{++} , and Bi^{+++} at both pH values, and the behavior of K^+ and Co^{++} at a pH of 11.2 only.

The cations which promote passivity at both pH values are Mg^{++} , Cu^{++} , Zn^{++} , Pb^{++} , Ni^{++} , and Ag^+ . The influence of Mg^{++} and Ni^{++} at a pH of 11.2 is very small, and it is hardly correct to say that the ions induce passivity. However, they do change the shape of the normal curve in this direction. At the lower pH, K^+ and Co^{++} are also passivating. Time-potential curves illustrating these effects are shown in Figs. 1 and 2.

Anions.—In order to present as complete a picture as possible, the effects of a few

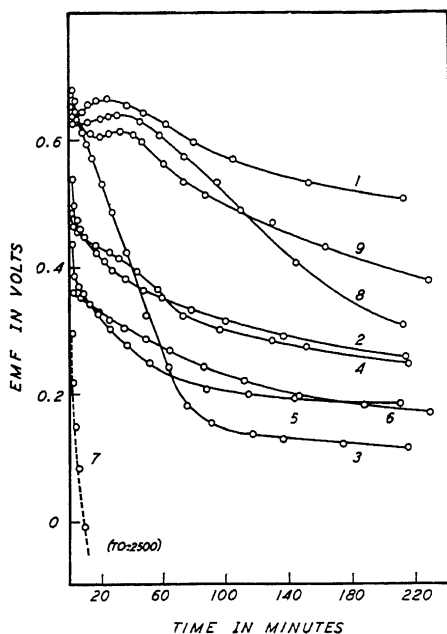


FIG. 2.—TIME-POTENTIAL CURVES SHOWING INFLUENCE OF ADDED CATIONS ON BEHAVIOR OF TIN IN CARBONATE SOLUTIONS WITH pH 8.4.

| | |
|---------------------------|---------------------------|
| Curve 1, Ca^{++} | Curve 6, Ni^{++} |
| Curve 2, Mg^{++} | Curve 7, Ag^+ |
| Curve 3, Cu^{++} | Curve 8, K^+ |
| Curve 4, Zn^{++} | Curve 9, Co^{++} |
| Curve 5, Pb^{++} | |

the normal curve. Arsenite ion is in class 2 of the previous paper;² it induces passivity at a pH below 10.0. Silicate is in class 3 in that it promotes passivity over the entire pH range studied. Sulphide ion requires a new classification in that it promotes activity throughout the pH range studied. The important time-potential curves for these ions are shown in Fig. 3.

Influence of Atmosphere.—A brief description of the influence of the atmosphere above the solution gives information on the mechanism of corrosion. To demonstrate this, an experiment was made in which the gas passed through the cell could be alter-

nated between tank oxygen and tank nitrogen. The time-potential curve in a solution with pH 11.2 is shown in Fig. 4. While nitrogen is being used, the metal is

makes the oxide film nonprotective. These effects set up a differential aeration cell in ordinary weight-loss experiments in which the lower part of the specimen, away from

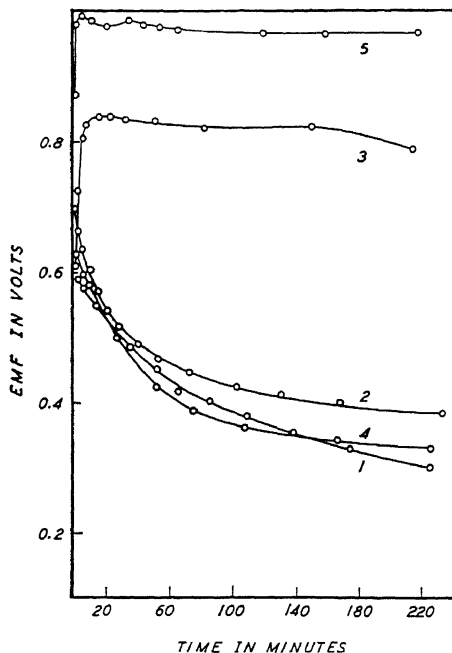


FIG. 3.—TIME-POTENTIAL CURVES SHOWING INFLUENCE OF ADDED ANIONS ON BEHAVIOR OF TIN IN CARBONATE SOLUTIONS.

Curve 1, 0.01 M Na_2HAsO_3 , pH 10.

Curve 2, 1.0 per cent Na_2SiO_3 , pH 11.2. (40°–42° Bé. Tech.)

Curve 3, 0.1 per cent Na_2SiO_3 , pH 11.2.

Curve 4, 0.1 per cent Na_2SiO_3 , pH 10.0.

Curve 5, 0.001 M Na_2S , pH 11.2.

abnormally active, with a steady potential of 0.98 volts. In changing to oxygen the gas was bubbled through the electrolyte for $\frac{1}{2}$ hr. and then maintained over the electrolyte in the normal manner. The potential falls off at once, and a steady value of 0.1780 volts was shown for a period of 3 days. When nitrogen was again admitted the potential rose rapidly to its previous value. Evidently the excess of oxygen stabilizes the stannic hydroxide corrosion product to the extent that it becomes protective. The total absence of oxygen caused by the introduction of nitrogen

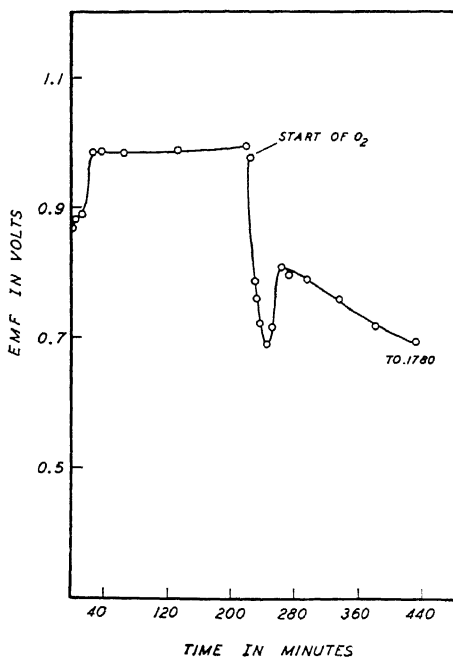


FIG. 4.—EFFECT OF OXYGEN AND NITROGEN ON THE TIME-POTENTIAL CURVE FOR CHEMPUR TIN IN CARBONATE SOLUTIONS, pH 11.2.

The system was under an atmosphere of nitrogen for the first 220 minutes; the atmosphere was then changed to oxygen.

atmospheric oxygen, becomes anodic to the upper part, where a protective film is formed.

Preparation and Selection of Alloys.—In examining the effects of alloying elements, a number of factors were considered in preparing the samples. The choice of alloying elements was not limited to those which might have commercial possibilities, since the principal object was to obtain a wide variety of data upon which to base general conclusions. The problem was confined to finding the effects of small amounts of alloying elements on the corrosion of tin, and examination of entire alloy systems did not seem pertinent. The compositions were

selected with the idea of obtaining a typical variety of structures from a given alloy system. For example, a hypoeutectic, a eutectic, and a hypereutectic composition lies so close to pure tin that the selection desired could not be made complete with any certainty. In other cases the eutectic composition was so far from the tin-rich

TABLE I.—*Compositions*

| Alloying Element, Per Cent | Alloy Type | Source of Element | Preparation |
|--|--|--|--|
| 0.4 Cu... 0.75 Cu... 1.0 Cu... 3.0 Cu... 5.0 Cu... | Hypoeutectic Eutectic Hypereutectic Hypereutectic Hypereutectic | { Chempur Sn 99.9919 % Sn O.F.H.C. Cu 99.9+ % Cu | { Melted in clay crucible under charcoal 19.71 per cent Cu master alloy |
| 0.1 Zn... 0.5 Zn... 2.0 Zn... 8.2 Zn... 10.0 Zn... 15.0 Zn... | Solid solution Hypoeutectic Hypoeutectic Hypoeutectic Hypereutectic Hypereutectic | { Chempur Sn Horse Head Special Zn 99.95 % Zn | { Melted in clay crucible under charcoal 24.37 per cent Zn master alloy |
| 0.1 Ni... 0.18 Ni... 0.50 Ni... | Hypoeutectic Eutectic Hypereutectic | { Chempur Sn Electrolytic Ni 99.95 % Ni | { Melted in clay crucible under charcoal 10.0 per cent master alloy |
| 0.1 Fe... 1.0 Fe... | Hypereutectic Hypereutectic | { Chempur Sn H ₂ purified Carbonyl Fe 99.95 % Fe | { Melted in clay crucible under charcoal 2.6 per cent master alloy |
| 0.1 Pb... 1.5 Pb... 3.0 Pb... 5.0 Pb... | Solid solution Solid solution Hypoeutectic Hypereutectic | { Chempur Sn and High Purity Pb 99.999 % Pb | { Melted in clay crucible under charcoal 24.98 per cent master alloy |
| 0.05 Ag... 0.1 Ag... 1.0 Ag... | Solid solution Hypoeutectic Hypoeutectic | { Chempur Sn and High Purity Ag 99.995 % Ag | { Melted clay crucible under charcoal 5.60 per cent Ag master alloy |
| 0.1 In... 1.0 In... 3.0 In... | Solid solution Hypoeutectic Hypoeutectic | { Chempur Sn and 99.986 % In | { Melted in clay crucible under charcoal 3 per cent master alloy |
| 0.1 Mg... 1.87 Mg... 2.5 Mg... | Hypoeutectic Eutectic Hypereutectic | { Chempur Sn and High Purity Mg 99.9 % Mg | { Melted in clay crucible under flux CaF ₂ , 40 grams; KCl, 320 grams; NaF, 60 grams; MgCl ₂ , 900 grams; 10 per cent master alloy |
| 0.5 Cd... 1.0 Cd... 2.5 Cd... | Solid solution Solid solution Hypoeutectoid | { Chempur Sn and 99.9 % Cd | { Melted in glass tubing under paraffin 2.5 per cent master alloy |
| 0.5 Sb... 1.0 Sb... 3.0 Sb... 6.0 Sb... | Solid solution Solid solution Solid solution ($\alpha + \beta$) | { Chempur Sn and 99.60 % Sb | { Melted in glass tubing under paraffin 6 per cent master alloy |
| 0.1 Bi... 0.5 Bi... 1.0 Bi... | Hypoeutectic Hypoeutectic Hypoeutectic | { Chempur Sn and Pharmaceutical Bi 99.98 % Bi | { Melted in clay crucible under charcoal 1 per cent master alloy. Melted in glass tubing under paraffin 1 per cent master alloy |
| 0.1 Ca... | Hypereutectic | { Chempur Sn and Commercial Pure Ca | { Melted in plumbago crucible under charcoal 1 per cent master alloy |
| High-purity Sn... | | Special preparation | { Melted in Al ₂ O ₃ crucible in vacuum. Estimated 99.9999 per cent pure |

were selected whenever possible. In some cases compositions within and without the terminal solid solution range were selected. In many systems the eutectic composition

side that an examination of other than hypo compositions was omitted. It is believed, however, that a sufficient variety has been studied to disclose any important generali-

ties that may exist. The compositions used are listed in Table 1. Most of the alloys were melted in clay crucibles under charcoal. Master alloys were prepared first, and

BEHAVIOR OF ALLOY

Potential measurements were made at the two extremes of the pH range only

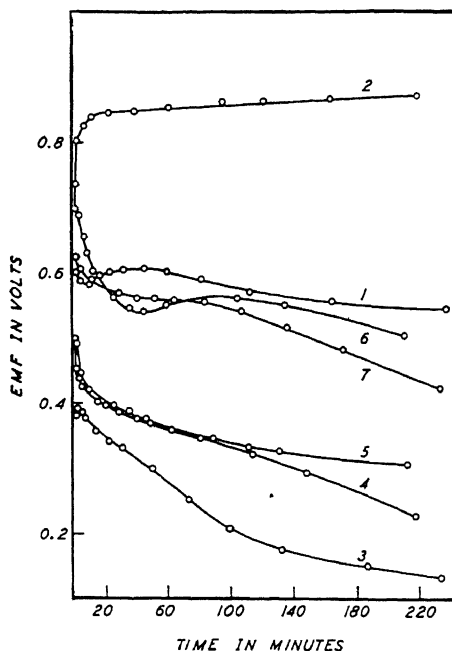


FIG. 5.—TIME-POTENTIAL CURVES FOR NORMAL ALLOYS IN CARBONATE SOLUTIONS.
Curve 1, 1.5 per cent Pb, pH 8.4.
Curve 2, 1.5 per cent Pb, pH 11.2.
Curve 3, 0.1 per cent Fe, pH 8.4.
Curve 4, 1 per cent Sb, pH 8.4.
Curve 5, 6 per cent Sb, pH 9.5.
Curve 6, 0.5 per cent Cd, pH 8.4.
Curve 7, 0.1 per cent Ni, pH 8.4.

the final samples were made from them. The composition was taken as that of the weighed elements, since exact values were not important. The structures were checked with those to be expected from the equilibrium diagram. In some special cases chemical analyses were made. Important exceptions to these generalities are listed in Table 1. The surfaces of the potential specimens were finally prepared as described previously,² except that the final vacuum anneal was always 10° below the eutectic temperature.

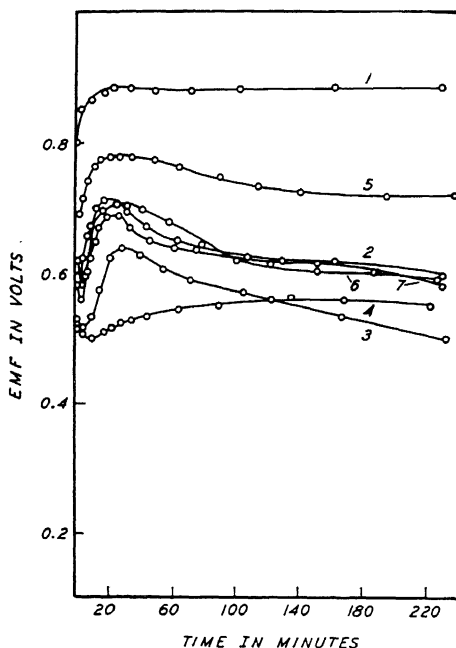


FIG. 6.—TIME-POTENTIAL CURVES FOR TIN-COPPER ALLOYS IN CARBONATE SOLUTIONS.
Curve 1, 0.75 per cent Cu, pH 11.2.
Curve 2, 0.75 per cent Cu, pH 10.0.
Curve 3, 0.75 per cent Cu, pH 9.5.
Curve 4, 0.75 per cent Cu, pH 8.4.
Curve 5, 3 per cent Cu, pH 10.0.
Curve 6, 3 per cent Cu, pH 9.5.
Curve 7, 0.4 per cent Cu, pH 10.0.

(pH 11.2 and 8.4) with intermediate values for a few cases of special interest. The results may be divided into three groups: (1) normal, (2) active, and (3) passive, and will be described in that order.

To establish the validity of using the curves obtained from a good grade of commercial tin as a standard of comparison, a series of measurements was made with a special grade of high-purity tin prepared in the laboratory for extrusion work.³ The material has been estimated as six nines pure. The potential curves for this do not

differ in any significant features from those already published for Chempur tin, although it seemed as though the final, steady, horizontal section of the curve is

this effect persists up to a pH of 9.5. These deviations from normality are shown in Fig. 5. The alloys have been classed as normal, to avoid confusing the general

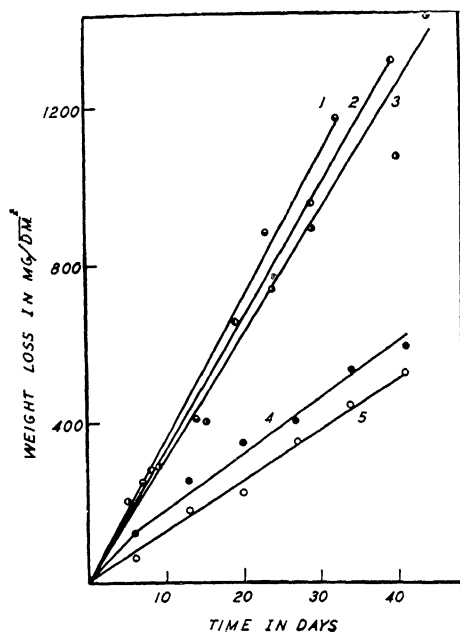


FIG. 7.—WEIGHT-LOSS OF TIN-COPPER ALLOYS AT pH 11.2 AND 10.0.

Curve 1, 5 per cent Cu alloy, pH 11.2.
Curve 2, 3 per cent Cu alloy, pH 11.2.
Curve 3, 0.75 per cent Cu alloy, pH 11.2.
Curve 4, 1.0 per cent Cu alloy, pH 10.0.
Curve 5, 0.75 per cent Cu alloy, pH 10.0.

reached more rapidly with the high-purity material.

1. *Normal.*—The alloying elements that do not change these normal curves markedly are Cd, Fe, Sb, Cu, Ag, Ni, Bi, and Pb. These include the commonest impurities in commercial grades of tin and substantiate the conclusion of the previous paragraph that small amounts of these impurities do not alter the corrosion characteristics of the material appreciably. It is necessary to add that Ag and Pb are the only ones of the elements listed that are entirely normal. At a pH of 8.4 the alloys with Sb, Cu, Cd, 0.1 and 0.18 per cent Ni, and 0.1 per cent Fe are passive, and with the 6 per cent Sb alloy

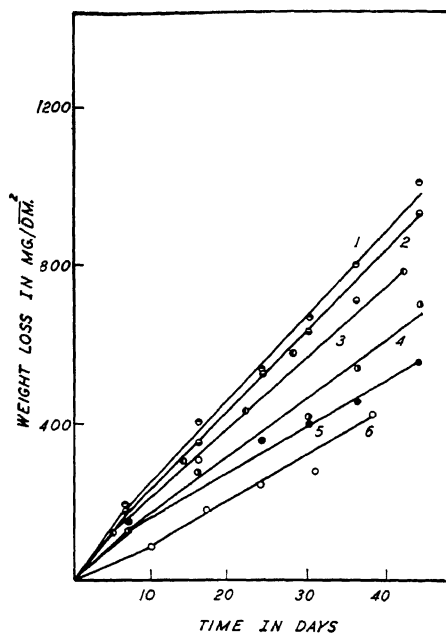


FIG. 8.—WEIGHT-LOSS OF ANTIMONY ALLOYS IN CARBONATE SOLUTIONS.

Curve 1, 6 per cent Sb alloy, pH 11.2.
Curve 2, 3 per cent Sb alloy, pH 11.2.
Curve 3, 1 per cent Sb alloy, pH 11.2.
Curve 4, 6 per cent Sb alloy, pH 10.0.
Curve 5, 3 per cent Sb alloy, pH 10.0.
Curve 6, 1 per cent Sb alloy, pH 10.0.

picture, and because even pure tin is not attacked appreciably at so low a pH.

The copper alloys are so widely used in practice that they were examined more completely. Some of the potential measurements are shown in Fig. 6. There are no striking effects, but some differences occur, which, combined with other information to be described later, indicate that it is desirable to keep the copper content below the eutectic composition of 0.75 per cent Cu. The passive tendency shown by tin and most of its alloys at the low pH of 8.4 is extended to somewhat higher pH values by the addition of small amounts of copper. At a pH of 9.5 or 10 the potential curves for a

3 per cent Cu alloy correspond very closely to those of tin, but the alloys with 0.75 per cent or less of copper all have somewhat lower values in this range. When the pH is

copper, the amount of corrosion increases with the alloy content, as well as with the pH of the solution. Under the conditions of the test the antimony alloys are somewhat

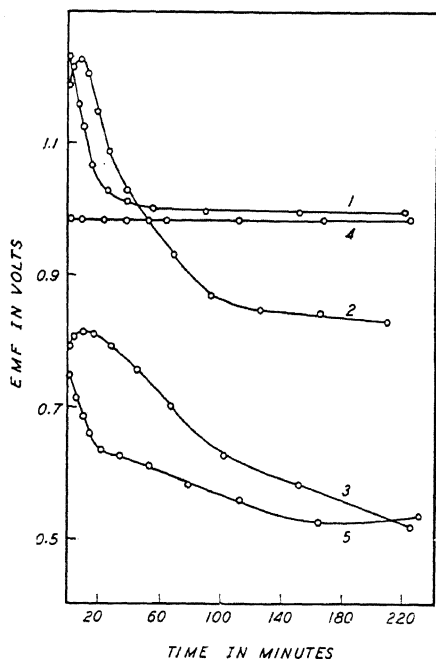


FIG. 9.—TIME-POTENTIAL CURVES FOR TIN-CALCIUM AND TIN-MAGNESIUM ALLOYS IN CARBONATE SOLUTIONS.

- Curve 1, 2.5 per cent Mg alloy, pH 11.2.
 Curve 2, 2.5 per cent Mg alloy, pH 8.4.
 Curve 3, 0.1 per cent Mg alloy, pH 8.4.
 Curve 4, 0.1 per cent Ca alloy, pH 11.2.
 Curve 5, 0.1 per cent Ca alloy, pH 8.4.

as high as 11.2, all of the alloys show normal curves except 5 per cent Cu, which is somewhat higher. Weight-loss data at a pH of 11.2 show that the influence of copper content is negligible under these conditions. However, at a pH of 10.0 this effect becomes better defined (Fig. 7). It is evident in all of these diagrams that the influence of pH is much greater than that of alloy composition in this series. However, if the pH is predetermined it should be possible to minimize corrosion by proper choice of composition.

Weight-loss curves have also been made for the antimony alloys (Fig. 8). As with

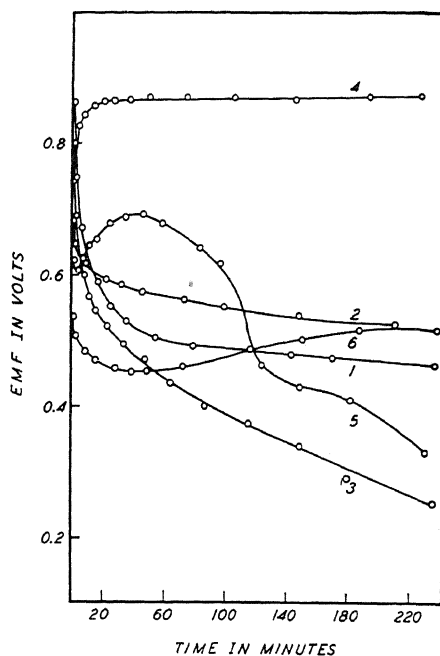


FIG. 10.—TIME-POTENTIAL CURVES FOR TIN-ZINC AND TIN-INDIUM ALLOYS IN CARBONATE SOLUTIONS.

- Curve 1, 0.1 per cent Zn alloy, pH 11.2.
 Curve 2, 0.1 per cent Zn alloy, pH 8.4.
 Curve 3, 15.0 per cent Zn alloy, pH 11.2.
 Curve 4, 0.1 per cent In alloy, pH 11.2.
 Curve 5, 1.0 per cent In alloy, pH 11.2.
 Curve 6, 0.1 per cent In alloy, pH 8.4.

superior to copper alloys. However, the corrosion product is a black, nonadherent material, which would be objectionable in most circumstances.

2. *Active*.—Of all the alloys studied, only those with the alkaline earths, magnesium and calcium, were more severely corroded than pure tin. At a pH of 11.2 the steady potential values of both materials are about 0.1 volt higher than normal, but the initial values are very much higher, and it may be presumed that the low solubility of the carbonates affords some protection to the metal. At a pH of 8.4 the Ca alloy and the

0.1 per cent Mg are definitely passive, but the two magnesium-rich alloys have unusually high initial and steady values (Fig. 9). These magnesium-rich alloys liberate hy-

drogen spontaneously from the carbonate solutions and disintegrate rapidly, in fact, after a few weeks exposure to the atmosphere they become very brittle. The 0.1 per cent Mg alloy, which contains all the magnesium in solid solution, does not have this tendency to become brittle. This behavior of magnesium alloys is comparable to that of tin-rich aluminum alloys.⁶

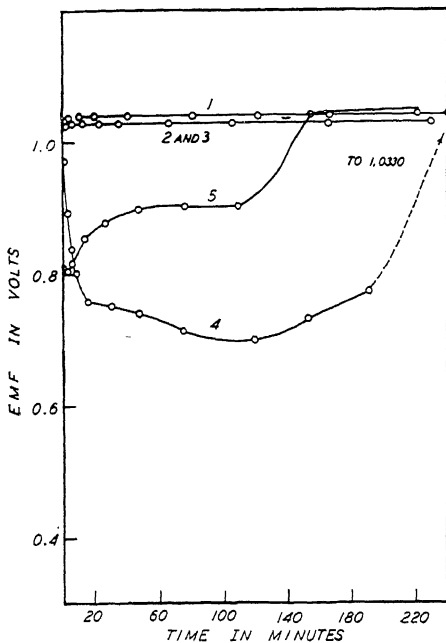


FIG. 11.—TIME-POTENTIAL CURVES FOR TIN-ZINC ALLOYS IN SODIUM HYDROXIDE SOLUTION pH 11.2.

Curve 1, 15 per cent Zn alloy.
Curve 2, 10 per cent Zn alloy.
Curve 3, 8 per cent Zn alloy.
Curve 4, 2 per cent Zn alloy.
Curve 5, 0.5 per cent Zn alloy.

drogen spontaneously from the carbonate solutions and disintegrate rapidly, in fact, after a few weeks exposure to the atmosphere they become very brittle. The 0.1 per cent Mg alloy, which contains all the magnesium in solid solution, does not have this tendency to become brittle. This behavior of magnesium alloys is comparable to that of tin-rich aluminum alloys.⁶

3. *Passive*.—The group of passive alloys includes zinc and indium, and they have been studied over the entire pH range. Since these alloys are important because of their ability to withstand corrosion in certain alkaline solutions, special attention

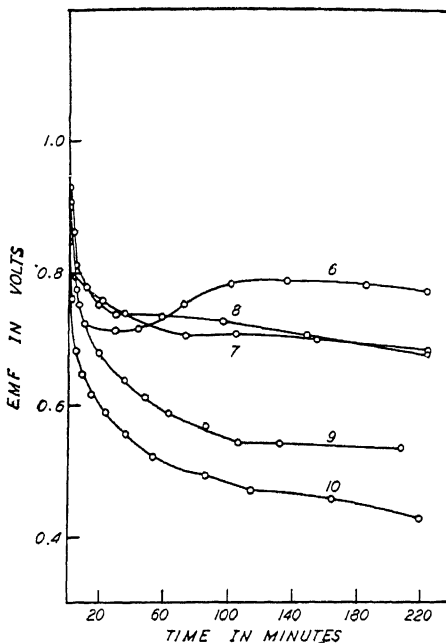


FIG. 12.—TIME-POTENTIAL CURVES FOR TIN-ZINC ALLOYS IN SODIUM HYDROXIDE SOLUTION, pH 8.4.

Curve 6, 8 per cent Zn alloy.
Curve 7, 15 per cent Zn alloy.
Curve 8, 10 per cent Zn alloy.
Curve 9, 2 per cent Zn alloy.
Curve 10, 0.5 per cent Zn alloy.

The potential measurements have been checked by weight-loss experiments with 1 and 3 per cent In alloys at pH 10 and pH 11.2, which were discontinued at the end of 110 days because no corrosion could be detected. Weight-loss experiments were made with the entire range of zinc alloys at a pH of 11.2 and these were discontinued at the end of 55 days because no corrosion had occurred. In carbonate-free solutions of pH 11.2 and 8.4 containing NaOH only, the series of zinc alloys remained passive in the solution of lower pH only (Figs. 11 and 12). This behavior of the zinc alloys indicates that a zinc carbonate film may be

responsible for inducing passivity in carbonate solutions, since passivity is absent in the NaOH solution of pH 11.2. In service tests, the Sn-Zn alloys withstood the corrosion of the alkaline products, but were subject to intergranular corrosion by the atmosphere. Neither the indium nor the zinc alloys appear to have commercial promise because the atmospheric corrosion of zinc is objectionable and indium must still be regarded as a precious metal.

4. *Oxide Films*.—The general importance of thin films in corrosion processes is well known. Most tin packages are baked at some time during their manufacture to facilitate drying of the lacquers used on the outside. Therefore, it seemed desirable to determine the effect of the alloys studied upon the atmospheric oxidation of the material, and also to determine the corrosion resistance of the oxide films thus formed. Two treatments were selected for this purpose: (1) baking for 50 min. at 105°C., which approximates the treatment generally used in practice; (2) baking for 5 hr. at 175°C. The second treatment produces a thicker film, generally in the temper color range, which it was felt might be better suited to the type of observations to be described. None of these samples showed a corrosion behavior markedly different from that of the unoxidized metal, but in many cases the steady potential value was attained slowly.

INTERPRETATION

Classification of Alloys.—The collection of corrosion data is relatively simple as compared to their correct interpretation. Nevertheless, an effort to derive as much information as possible from such data is usually in order. A general division of the alloys studied into good, bad, and indifferent groups may be made from the classification into passive, active, and normal groups, which already has been made on the basis of the potential measurements. Zinc and indium may be considered as good over

the entire pH range, magnesium and calcium are definitely bad, and the other metals are indifferent except that some of them do reduce corrosion at lower pH values. The weight-loss data are in general agreement with the potential measurements and also show that antimony, even though it does not prevent corrosion, causes less corrosion than copper. Also, pure tin is more resistant to corrosion than the alloys with the bad or indifferent metals, but less resistant than its alloys with indium or zinc.

Influence of Structure.—The alloy compositions were selected so as to give as great a variety of structures as possible. The results do not point to any important general influence of this factor. Wherever the corrosion characteristics change with composition, they seem to change in proportion to the amount of alloy element present, with no sharp changes as one passes from a hypoeutectic to a hyper-eutectic alloy. When solid solution occurs, the results are somewhat more surprising, and it may be that more accurate studies would reveal a sharp change when the solid solubility of the system is passed. The recent work of Brown, Fink, and Hunter⁴ bears out this point. The determinations of solid solubility at room temperature are somewhat uncertain and in view of the extremely limited range in most tin alloys, it may be that some of the alloys have not been classified properly. However, it seems quite certain that the alloys containing 0.5 per cent, 5 per cent, 1.0 per cent, and 3.0 per cent Sb are within the solid solution range and the changes in corrosion resistance seem to be quite regular right on up to the two-phase 6 per cent Sb alloy.

Periodic Relations.—Checking the elements used as alloy additions upon a periodic table offers an opportunity to judge the influence of atomic structure upon corrosion of alloys. The series Ag, Cd, Sn, In, Sb have atomic numbers 47-51, and the new electrons are filling in the outer

fifth quantum group in order. Additions of Ag have no influence on the potential behavior of Sn, but both Cd and Sb promote passivity at a low pH, while In induces passivity at a high pH also. In the series Fe, Ni, Cu, Zn the same general observations apply and as the structure of the atom becomes more like that of Sn, the corrosion resistance of the alloy increases. The alkaline earths Mg and Ca are far removed from Sn in the table and their alloys are readily attacked. The heavier metals Pb and Bi are very similar to Sn in structure and do not alter its corrosion properties greatly. Though this analysis does not explain why In and Zn promote passivity, it does indicate the desirability of alloying with chemically similar elements.

Influence of Position in Electromotive Series.—The position of the elements in the electromotive series is important and must be included in the interpretation of the results of the present work. The addition of alloying elements may change the electrochemical potentials of the alloy so as to affect the current flow between local elements. With tin, where very few elements alloy with it to form solid solutions, the general case finds the alloys of tin consisting of two constituents. If the second phase is less noble than the tin, local areas will differ electrochemically, setting up small cells and thus increasing the rate of corrosion. This also applies to phases that are nobler than tin. Where the alloying elements are electrochemically similar, small cells may be formed but the currents are reduced to small values and the corrosion rate is not appreciably changed.

The elements classed as normal in a previous section (Cd, Fe, Sb, Cu, Ag, Ni, Pb, and Bi) all lie reasonably close to Sn in the electromotive series except Ag. Although each of these elements shows a potential curve similar to that of Sn, weight-loss measurements would perhaps reveal that all these elements increase the

corrosion rate of Sn as shown for the Sn-Cu alloys. The elements classed as active (Mg and Ca) differ greatly from Sn electrochemically and, as expected, increase the corrosion rate tremendously. The passive class of elements (In and Zn) are situated near Sn in the series. However, passivity cannot be directly attributed to the position of these two elements in the series, but their nearness to Sn would be an advantage and would be one of the contributing factors in producing passivity.

With respect to the cations in solution, something may be said about the influence of their position in the e.m.f. series. The cations of metals that are cathodic to tin should plate out on to the surface of the tin, rendering it passive if the coating possesses the proper characteristics. Likewise, the ions of metals that are anodic to tin will tend to remain in solution. Of the cations producing passivity, Cu^{++} , Ag^+ , and Pb^{++} are the most prominent and are cathodic to Sn. But Mg^{++} , Zn^{++} , and Ni^{++} , which also produce passivity, are anodic to Sn and their influence cannot be explained by such reasoning. However, their passivating tendency is very weak compared with Cu^{++} and Ag^+ . In the other class of cations (normal) all the elements are anodic to Sn except Bi^{+++} , and no film formation should be expected.

Of all the elements, only zinc acting as an alloying agent and also as a cation in solution produces the same effect. With all others, no similar relationship exists. Such an element as Mg, which is far removed from Sn anodically, in the e.m.f. series induces passivity as Mg^{++} but is harmful as an alloying element. Cu and Ag, which are cathodic to Sn, increase corrosion resistance as Ag^+ and Cu^{++} but are not beneficial as alloying elements, because the ions do not enter the corroding medium; these metals are in the cathodic areas of the alloy, and cannot build up a protective film.

There are other factors that influence the corrosion properties of tin and its alloys, which have not been considered in this paper. Grain size⁵ has been shown to have some effect on the amount of corrosion of tin in carbonate solutions; the finer the grains, the less the corrosion. However, since most of the alloying elements tend to reduce the grain size of tin, it is difficult to isolate the effect of grain size from the data presented. Other factors, such as solubility of the corrosion product and hydrogen over-voltage of the alloy phases, naturally should influence the corrosion characteristics of tin in alkaline solutions. It will be necessary to obtain more experimental data before these factors can be discussed.

SUMMARY

1. Time-potential curves have been made for the following cations in sodium carbonate solutions of pH 11.2 and 8.4; K^+ , Li^+ , NH_4^+ , Ca^{++} , Fe^{++} , Cd^{++} , Mn^{++} , Ba^{++} , Bi^{+++} , Co^{++} , Mg^{++} , Cu^{++} , Pb^{++} , Zn^{++} , Ni^{++} , Ag^+ , and In^{+++} . Of these, Mg^{++} , Ag^+ , Pb^{++} , Cu^{++} , Zn^{++} , Ni^{++} promoted passivity.

2. Arsenate, arsenite, silicate and sulphide ions have been added to sodium carbonate solutions of pH 11.2 and 10.0; silicate caused passivity in this range.

3. The effect of oxygen and nitrogen on the corrosion of tin has been studied. Oxygen induces passivity, while nitrogen increases the corrosion rate.

4. Measurements over the entire pH range of carbonate solutions show little

difference between tin of very high purity and Chempur tin.

5. Time-potential curves have been made for binary tin alloys containing the following elements; Cu, Zn, Ni, Fe, Pb, Ag, In, Mg, Cd, Sb, Bi, and Ca. Weight-loss measurements in selected cases, Cu, Zn, Sb, and In, alloyed with Sn were made, and measurements were of the order predicted by the time-potential curves. Zn and In were the most effective in reducing corrosion.

6. Films developed by heating the various alloys at temperatures of 105°C. for 50 min. and 175°C. for 5 hr. provided no additional protection to the alloys in the alkaline solutions.

ACKNOWLEDGMENT

The Bristol-Myers Co., of New York City, and the Sun Tube Corporation, of Hillside, N. J., have sponsored the research program of which this investigation is a part.

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Effect of Composition on Physical and Chemical Properties of 14-karat Gold Alloys

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(Cleveland Meeting, October 1940)

IN 14-karat gold alloys, as in 10-karat gold alloys,³ the addition of such metals as zinc, nickel, copper and silver produces a wide range of physical and chemical properties such as color, hardness, corrosion resistance and melting points. These important factors made gold alloys desirable in the optical work and for jewelry.

In 14-karat gold alloys, as well as in 10-karat or 12-karat, it is possible to have two golds of the same color, one of which will corrode more than the other, although it may be harder. Some of these alloys have been investigated by F. E. Carter,¹ E. M. Wise,⁵ and L. Sterner Rainer.⁴

In this group of alloys the gold content of 58.3 per cent (14-karat) was held constant, while the copper varied from 36 to 24 per cent. The balance of the alloy consisted of one, two, or three of the metals silver, zinc, and nickel.

All the alloys were melted in an induction furnace and cast into an ingot that measured 3 by $\frac{1}{4}$ by $\frac{3}{4}$ in. The method of determining the melting points, color determinations and acid test have been discussed in previous papers by the author.^{2,3}

It is necessary to use small test bars (Fig. 1). The tensile bars were annealed at 1300°F. for 20 min. and then air-cooled. There being a very marked drop when the yield point was reached, "the drop of the beam" method was used in determining the yield point.

ALLOYS

Gold-copper-zinc Alloys.—Gold-copper-zinc alloys melt, cast, and fabricate easily. The low melting points, however, limit

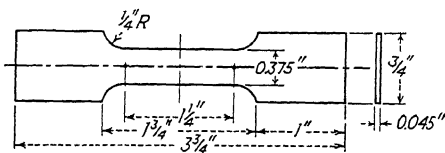


FIG. 1.—TEST BAR.

their use to some extent. The physical properties of these alloys are not entirely satisfactory. When the ultimate strength is satisfactory, the elongation and reduction of area are too low (Table 1).

Gold-copper-zinc-nickel Alloys.—In this group of alloys, in which zinc and nickel replace copper in approximately equal parts (Table 1), the yield point, hardness, and ultimate strength increase with the increase of zinc and nickel content, while the reduction of area and elongation decrease. The physical properties are desirable, particularly of the white gold alloys. The alloys of this group are not difficult to cast and fabricate, and most of these colors could be used commercially.

Gold-copper-nickel Alloys.—Gold-copper-nickel alloys are similar to the gold-copper-zinc and the gold-copper-zinc-nickel alloys. They do, however, possess high yield point, ultimate strength and hardness, somewhat higher than those of the other two groups mentioned (Table 1). The difficulty with these alloys is that they fire-crack readily and heavy rolling is necessary between annealings. Being hard to fabricate, many

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³ References are at the end of the paper.

TABLE I.—Physical Properties of Alloys

| No. | Color | Composition of Alloy, Per Cent | | | | Corrosion Loss, Grams per Sq. In. | Melting Point, Deg. F. | Yield Point, Lb. per Sq. In. | Ultimate Strength, Lb. per Sq. In. | Elongation, Per Cent in $\frac{1}{4}$ In. | Reduction of Area, Per Cent | Hardness, Rockwell B Scale |
|-----|-------|--------------------------------|--------|--------|------|-----------------------------------|------------------------|------------------------------|------------------------------------|---|-----------------------------|----------------------------|
| | | Gold | Silver | Copper | Zinc | Nickel | | | | | | |

| | | | | | | | | | | | | |
|---------------------------------------|----------------|------|------|-------|-------|-------|------|--------|---------|------|------|-----|
| GOLD-COPPER-ZINC SERIES | | | | | | | | | | | | |
| 3 | Orange yellow. | 58.3 | | 35.74 | 5.96 | | 1675 | 24,000 | 54,400 | 60.0 | 42 | 42 |
| 6 | Brass yellow. | 58.3 | | 32.86 | 8.84 | | 1650 | 23,200 | 55,800 | 65.0 | 44.5 | 42 |
| 9 | Brass yellow. | 58.3 | | 30.90 | 10.8 | | 1620 | 22,400 | 55,000 | 67.5 | 45.0 | 40 |
| 12 | Brass yellow. | 58.3 | | 29.02 | 12.68 | | 1605 | 20,300 | 56,000 | 62.5 | 44.0 | 40 |
| 15 | Brass yellow. | 58.3 | | 27.32 | 14.38 | | 1575 | 45,500 | 66,000 | 40.0 | 31.3 | 75 |
| 18 | Brass yellow. | 58.3 | | 24.86 | 16.84 | | 1530 | 50,000 | 70,000 | 27.5 | 26.4 | 78 |
| GOLD-COPPER-ZINC-NICKEL SERIES | | | | | | | | | | | | |
| 2 | Red pink. | 58.3 | | 35.59 | 2.94 | 3.17 | 1745 | 34,000 | 66,600 | 62.5 | 44.0 | 55 |
| 5 | Pale pink. | 58.3 | | 33.57 | 4.00 | 4.13 | 1750 | 36,000 | 70,000 | 61.5 | 42.0 | 60 |
| 8 | Pale pink. | 58.3 | | 31.27 | 5.18 | 5.25 | 1750 | 38,000 | 73,100 | 60.0 | 41.0 | 70 |
| 11 | Pale pink. | 58.3 | | 29.19 | 6.13 | 6.38 | 1750 | 41,100 | 76,000 | 60.0 | 41.0 | 71 |
| 14 | Yellow white. | 58.3 | | 27.35 | 7.51 | 6.84 | 1740 | 42,000 | 77,100 | 57.5 | 41.0 | 75 |
| 17 | White. | 58.3 | | 25.22 | 7.89 | 8.59 | 1715 | 45,600 | 87,200 | 50.0 | 38.0 | 83 |
| GOLD-COPPER-NICKEL SERIES | | | | | | | | | | | | |
| 1 | Light pink. | 58.3 | | 35.45 | | 6.25 | 1820 | 42,100 | 80,000 | 50.0 | 37.2 | 76 |
| 4 | Light pink. | 58.3 | | 33.27 | | 8.43 | 1830 | 46,500 | 82,000 | 37.5 | 35.0 | 80 |
| 7 | Pink white. | 58.3 | | 31.11 | | 10.59 | 1855 | 52,000 | 83,300 | 30.0 | 30.6 | 81 |
| 10 | White. | 58.3 | | 29.19 | | 12.51 | 1880 | 66,100 | 103,000 | 30.5 | 28.0 | 93 |
| 13 | White. | 58.3 | | 27.10 | | 14.54 | 1895 | 73,500 | 110,000 | 20.0 | 26.5 | 95 |
| 16 | White. | 58.3 | | 24.66 | | 17.94 | 1920 | 77,200 | 113,300 | 15.0 | 15.3 | 97 |
| GOLD-SILVER-COPPER-ZINC SERIES | | | | | | | | | | | | |
| 21 | Red pink. | 58.3 | 2.58 | 36.28 | 2.84 | | 1690 | 35,000 | 61,000 | 60.0 | 42.0 | 55 |
| 24 | Yellow. | 58.3 | 4.25 | 33.45 | 4.00 | | 1645 | 35,500 | 60,500 | 62.5 | 43.3 | 58 |
| 27 | Yellow. | 58.3 | 4.97 | 31.27 | 5.40 | | 1615 | 34,400 | 61,000 | 62.5 | 43.3 | 59 |
| 30 | Yellow. | 58.3 | 5.87 | 29.15 | 6.68 | | 1605 | 36,000 | 59,300 | 61.0 | 44.0 | 60 |
| 33 | Yellow. | 58.3 | 7.09 | 26.94 | 7.67 | | 1585 | 38,000 | 60,000 | 60.0 | 42.0 | 62 |
| 36 | Yellow. | 58.3 | 8.22 | 25.10 | 8.38 | | 1545 | 38,600 | 57,300 | 57.5 | 42.0 | 63 |
| GOLD-SILVER-COPPER-ZINC-NICKEL SERIES | | | | | | | | | | | | |
| 20 | Orange pink. | 58.3 | 2.0 | 35.05 | 1.85 | 2.20 | 1740 | 38,000 | 66,600 | 57.5 | 44 | 64 |
| 23 | Pale pink. | 58.3 | 2.71 | 32.27 | 3.92 | 2.80 | 1730 | 41,100 | 70,000 | 57.5 | 42.0 | 67 |
| 26 | Light pink. | 58.3 | 3.30 | 31.00 | 3.87 | 3.53 | 1720 | 43,800 | 71,300 | 58.0 | 42.6 | 72 |
| 29 | Light pink. | 58.3 | 3.96 | 28.56 | 4.97 | 4.21 | 1730 | 47,300 | 75,800 | 57.5 | 42.0 | 75 |
| 32 | Yellow white. | 58.3 | 4.71 | 27.02 | 5.59 | 4.38 | 1710 | 54,000 | 80,200 | 53.6 | 42.6 | 78 |
| 35 | Yellow white. | 58.3 | 5.50 | 24.90 | 5.80 | 5.50 | 1695 | 66,000 | 83,600 | 52.5 | 42.6 | 86 |
| GOLD-SILVER-COPPER-NICKEL SERIES | | | | | | | | | | | | |
| 19 | Pink. | 58.3 | 3.25 | 35.69 | | 2.76 | 1745 | 46,800 | 75,800 | 47.0 | 41.0 | 77 |
| 22 | Pale pink. | 58.3 | 3.84 | 33.73 | | 4.13 | 1745 | 51,000 | 80,000 | 45.4 | 35.0 | 81 |
| 25 | Pink. | 58.3 | 4.91 | 31.57 | | 5.22 | 1740 | 82,600 | 82,600 | 41.0 | 36.0 | 87 |
| 28 | Pale pink. | 58.3 | 5.93 | 29.10 | | 6.67 | 1740 | 70,100 | 91,300 | 35.0 | 30.0 | 90 |
| 31 | Yellow white. | 58.3 | 7.34 | 26.94 | | 7.42 | 1750 | 86,100 | 110,000 | 17.5 | 16.0 | 100 |
| 34 | Pink. | 58.3 | 8.19 | 24.84 | | 8.67 | 1745 | 88,700 | 110,000 | 7.5 | 8.0 | 103 |

of them cannot be used as commercial golds.

Gold-silver-copper-zinc Alloys.—In this group of alloys, in which the silver and zinc are present in approximately equal proportions, the physical properties show little change as the percentage of silver and zinc increases (Table 1). The physical properties in this group are more desirable than those of the gold-copper-zinc alloys. These alloys process easily and may be used as commercial gold.

Gold-silver-copper-zinc-nickel Alloys.—In this group of alloys, with three elements replacing copper in approximately equal proportions, the yield point and ultimate strength increase as the content of silver, zinc and nickel increases. Reduction of area remains fairly constant with the increase of silver, zinc and nickel, while the elongation decreases after 12 per cent addition of silver, zinc and nickel has been reached (Table 1). These alloys, possessing good physical properties, fabricate easily, making them usable as commercial gold alloys.

Gold-silver-copper-nickel Alloys.—The yield point, hardness and ultimate strength increase in gold-silver-copper-nickel alloys as the silver and nickel content increases, while the elongation and reduction of area decrease (Table 1). A few of these alloys may be used commercially, but most of them are difficult to cast and fabricate.

DISCUSSION OF PROPERTIES

The presence of silver in the 14-karat alloys brings about a slight change in corrosion loss (Table 1). The total corrosion loss for similar alloys in the 14-karat golds is far

less than for the 10-karat gold alloys.³ This change is brought about by the increase of gold content and was expected, as it is well established that the corrosion loss decreases as the gold content increases. The effect of silver in the alloy, however, is not marked in the 14-karat gold alloys as in the 10-karat groups, and this may be owing to the presence of a greater gold content.

Nickel plays the same part in the 14-karat gold alloys as it does in the 10-karat;³ that is, it helps to reduce corrosion loss and increases the hardness, yield point and tensile strength. Zinc acts in just the opposite way in these alloys, as it reduces the hardness, yield point and ultimate strength.

The effects of silver, zinc, and nickel are not as noticeable in the 14-karat gold alloys as in the 10-karat series. Corrosion loss is very low and the resistance to hydrogen sulphide is far greater than in 10-karat golds.

This group of alloys does not have as many marked changes as the 10-karat group. It is known that the intermetallic compounds formed in these alloys have an important influence on the properties of the alloys.

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Beneficial Effects of Zirconium in Cast Nickel-silicon Bronzes

By F. R. HENSEL,* MEMBER A.I.M.E., E. I. LARSEN,* AND A. S. DOTY*

(Chicago Meeting, October 1939)

THE alloy under discussion is a nickel-silicon bronze and is one of many age-hardening or precipitation-hardening

Fig. 1 shows results of heat-treating tests on two typical nickel-silicon bronze castings of the type on which the observations were

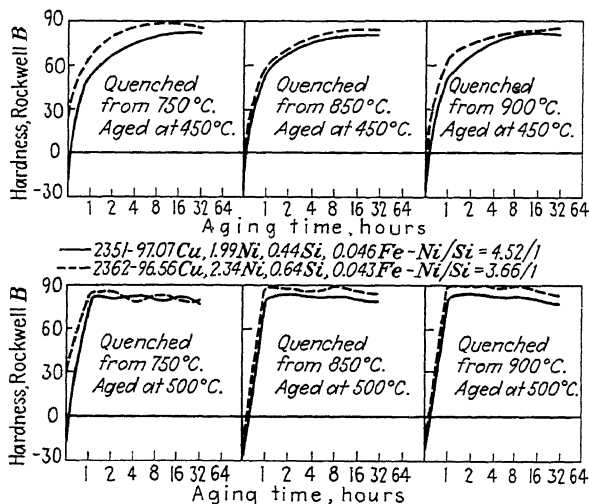


FIG. 1.—EFFECT OF QUENCHING AND AGING TEMPERATURES ON HARDNESS OF TWO TYPICAL NICKEL-SILICON BRONZES, NO. 2351 AND NO. 2362.

copper-base alloys. The hardening constituent is a nickel-silicon compound.¹ The quenching temperature necessary to produce hardening by a subsequent aging treatment is a function of the composition and extends from about 700°C. to 950°C.; the aging temperature range extends from 400° to 600°C.

The work carried out by the authors of this paper was confined to cast alloys having compositions within the ranges of: 1.5 to 3.00 per cent Ni; 0.4 to 0.75 per cent Si; balance, copper.

A quenching temperature of 750°C. produces almost as high a hardness on subsequent aging as do quenching temperatures of 850° and 900°C.

Several foundries have spent years of active and intelligent effort in trying to control the casting and heat-treating variables of nickel-silicon bronzes and finally gave up the attempts because of the inconsistencies of results.² This undesirable characteristic was not manifest in the ultimate hardness or conductivity but primarily in tensile strength and ductility, as shown in Table 1. The variation in tensile properties was often much greater than that existing on the alloys

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¹ References are at the end of the paper.

of Table 1. This table is shown because these eight test bars were from successive heats of the alloy made under conditions duplicated as closely as possible by the best modern foundry practice. In some instances test bars actually broke during machining.

TABLE 1.—*Characteristics of Cast Nickel-silicon Bronzes*

| Specimen No. | Hardness, Rockwell B | Electric Conductivity, Per Cent I.A.C.S. | Tensile Strength, Lb. per Sq. In. |
|--------------|----------------------|--|-----------------------------------|
| 2646 | 91 | 39.2 | 23,800 |
| 2647 | 89 | 40.1 | 29,200 |
| 2648 | 91 | 39.7 | 23,800 |
| 2649 | 90 | 39.7 | 51,200 |
| 2660 | 94 | 38.0 | 45,800 |
| 2661 | 96 | 37.7 | 48,200 |
| 2662 | 89 | 38.6 | 38,700 |
| 2663 | 90 | 38.3 | 21,800 |

In an effort to trace the cause of the trouble, various melting and casting techniques were employed. The Ni_2Si content was varied from 1.5 to 5 per cent and the nickel-silicon ratio varied from 3 to 1 to 6.5 to 1. No appreciable advantage or disadvantage was noted. In order to eliminate the trouble, additions were made of magnesium, beryllium, cadmium, zinc, manganese, phosphorus, iron, lithium, titanium, thorium, uranium and zirconium. Most of the additions were below 0.25 per cent. Certain single tests, such as 0.25 per cent Cd, 0.25 per cent Mg, 0.25 per cent Th and 0.1 per cent Mn, indicated some improvement, but continued investigation of the alloys still showed inconsistencies in regard to tensile strength.

Out of all the elements added in an attempt to improve the tensile strength of nickel-silicon bronze castings, zirconium alone gave consistently effective results. Test bars from at least 20 successive production heats to which approximately 0.25 per cent Zr was added showed no ultimate tensile strength below 56,000 lb. per sq. in. The average was about 65,000 and some tests showed over 70,000. In

comparison with tests on straight nickel-silicon bronze castings, which showed an average of only about 50,000 lb. per sq. in., with probably 35 per cent of the test bars

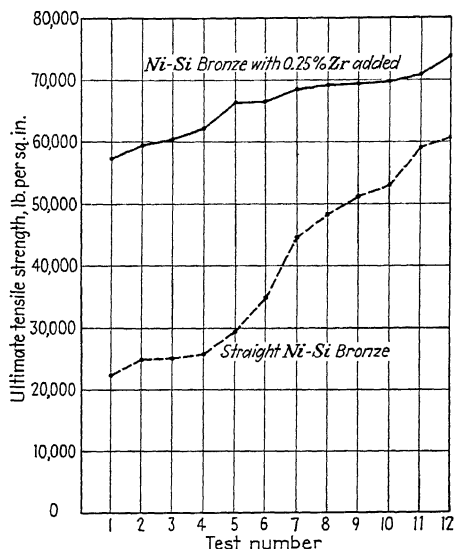


FIG. 2.—TENSILE STRENGTH OF TEST BARS FROM FIRST TWELVE PRODUCTION HEATS WITH 0.25 PER CENT ZIRCONIUM ADDED, COMPARED WITH TWELVE SUCCESSIVE HEATS OF NICKEL-SILICON BRONZE.

having less than 35,000 lb. per sq. in. ultimate tensile strength, a remarkable advantage was noted in the addition of zirconium.

Fig. 2 gives a graphic illustration of the tensile strength of test bars from the first 12 production heats to which 0.25 per cent Zr was added as compared with 12 successive heats of straight nickel-silicon bronze. The test results are arranged in order of increasing tensile strengths. This graph clearly shows the distinct improvement brought about by the additions of zirconium. Not only is the average strength considerably higher, but, more important, there are no test bars showing a tensile strength below 55,000 lb. per sq. in., whereas about 35 per cent of the tests on straight nickel-silicon bronzes show an ultimate tensile strength below 35,000 lb.

per sq. in. and only 15 per cent above 55,000 lb. per sq. inch.

strengths. Variation of the zirconium content from as little as 0.1 per cent up to



FIG. 3.

FIG. 3.—STRAIGHT NICKEL-SILICON BRONZE AFTER QUENCHING FROM 900°C. AND AGING 16 HOURS AT 450°C. $\times 75$.

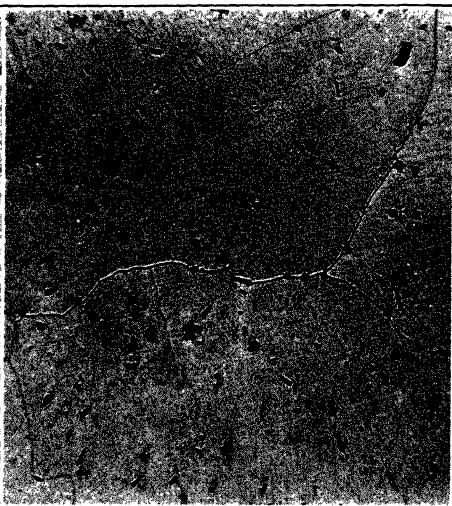


FIG. 4.

Note segregation in grain boundaries. Sample was polished, then etched in $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. FIG. 4.—NICKEL-SILICON BRONZE CONTAINING 0.28 PER CENT ZIRCONIUM AFTER SAME TREATMENT. $\times 75$.

Although some segregation is evident, it is not continuous nor nearly as pronounced as in Fig. 3. Sample was polished, then etched in $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.

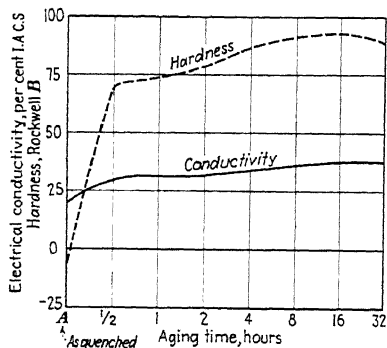


FIG. 5.—ELECTRICAL CONDUCTIVITY AND HARDNESS VERSUS AGING TIME.

Sample L-894-A quenched from 900°C., aged at 450°C. Nickel-silicon bronze with 0.25 per cent Zr added. Sand-cast.

Electrical conductivity sample, $\frac{3}{8}$ -in. diameter by 6 in.; hardness sample, 1 by 1 by $\frac{1}{2}$ inch.

In addition to test bars from production heats, several test bars from small experimental melts showed equally good tensile

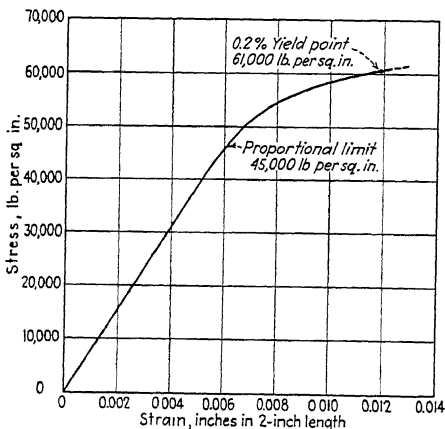


FIG. 6.—STRESS VERSUS STRAIN.

Nickel-silicon bronze with 0.25 per cent Zr added. Sand-cast. Ultimate tensile strength, 68,550 lb. per sq. in. Sample L-917-1.

1 per cent did not affect the results. Figs. 3 and 4 offer a possible explanation of the beneficial effects of zirconium.

In all tests with additions from 0.08 per cent up to 0.73 per cent Zr the grain boundaries were relatively fine and free from excessive segregation.

The addition of zirconium had no ill effects on the hardness and electrical conductivity of the alloys.

Fig. 5 shows typical aging curves on a nickel-silicon bronze to which 0.25 per cent Zr was added. Hardness reaches a maximum of approximately 90 Rockwell B after 16 hr. at 450°C. and conductivity reaches approximately 37 per cent I.A.C.S. after the same length of time. Fig. 6 shows a stress-strain curve on the same alloy. Ultimate tensile strength was 68,550 lb. per sq. in.; yield strength at 0.2 per cent elongation, 61,000 lb. per sq. in.; proportional limit, 45,000 lb. per sq. inch.

The information presented in this paper is primarily a résumé of factual data. The research work concerning the theoretical explanations is not complete. As mentioned before, the microstructure of the straight nickel-silicon bronzes indicates that the extreme brittleness is in some way connected with the type and location of the precipitate found during aging after quenching. Possibly the presence of zirconium—which in itself, or in combination with another element, can be used as a precipitation-hardening constituent in cop-

per—may alter the precipitate (either in respect to type or location) sufficiently to eliminate the intercrystalline weakness and general embrittlement found in cast nickel-silicon bronzes. Furthermore, zirconium is a most efficient degasifying agent, producing castings free from gases usually occluded within the grain boundaries. It seems quite possible that occluded gases may be the cause of incipient cracks during heat-treating. Another advantage of the zirconium addition was the effect on the formation of nuclei by zirconia, resulting in a finer grain structure.

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Study of the Metallography and Certain Physical Properties of Some Alloys of Cobalt, Iron, and Titanium

BY CHARLES R. AUSTIN* AND CARL H. SAMANS,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1940)

It has been known for several years¹ that certain alloys of the Konal type, containing commercial cobalt (99.32 per cent Co and 0.42 per cent Ni) and varying amounts of

tested at 600°C. are summarized in the upper section of Fig. 1. Similar specimens that were aged at 650°C. for 72 hr., after quench and prior to testing at 600°C., gave the results shown in the lower section of Fig. 1.

TABLE I.—Analysis of Material

| Constituent | Percentages | | |
|---------------------------------------|-------------|-------------|-------------|
| | Sample 3125 | Sample 3124 | Sample 3123 |
| Si..... | 0.25 | 0.51 | 0.60 |
| Fe..... | 4.15 | 10.70 | 13.17 |
| Ti..... | 1.15 | 3.58 | 4.70 |
| Mn..... | 0.30 | 0.41 | 0.42 |
| Co (by difference) ^a | 94.15 | 84.80 | 81.11 |

^a The cobalt from all three samples, united and tested for nickel, gave 0.54 per cent Ni based on the weight of cobalt.

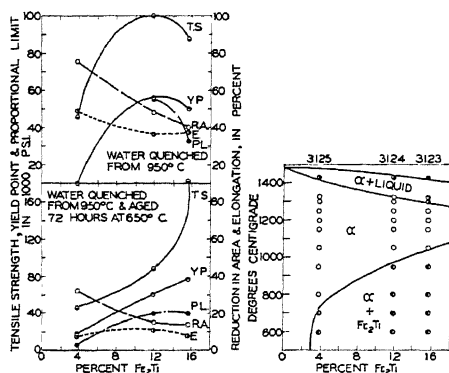


FIG. 1.

FIG. 1.—EFFECT OF VARYING AMOUNTS OF FERROTITANIUM (Fe_2Ti) ON PHYSICAL PROPERTIES OF COMMERCIAL COBALT. (C. R. Austin.¹)

Upper section. Tested at 600°C. after water-quenching from 950°C.

Lower section. Tested at 600°C. after water-quenching from 950°C. and aging 72 hr. at 650°C.

FIG. 2.—PORTION OF QUASI-BINARY DIAGRAM COBALT- Fe_2Ti AS DETERMINED METALLOGRAPHICALLY.

ferrotitanium, exhibit very high tensile strengths at 600°C. However, their proportional limits and yield points are relatively low. Published data¹ for the alloys quenched in water from 950°C. and then

In the present work the investigation of the properties of these materials has been extended by a study of the tensile deformation characteristics in moderately long-time tests at 600°, 700° and 800°C. after quenching from various solution temperatures. In addition, some metallographic studies have been made to correlate with the deformation tests, and to obtain information on the quasi-binary system cobalt- Fe_2Ti .

The material, very kindly furnished by the Westinghouse Electric and Manufacturing Co. in the form of hot-swaged rods of $\frac{3}{16}$ -in. diameter, analyzed as shown in Table I.

The alloys, when originally made up,¹ were based upon an iron-titanium compound, Fe_3Ti , as indicated by the work of

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* Professor and Associate Professor of Metallurgy, respectively, The Pennsylvania State College, State College, Pa.

¹ References are at the end of the paper.

J. Lamort,² W. Koester and W. Geller,³ and W. Jellinghaus.⁴ The more recent studies of H. Witte and H. J. Wallbaum⁵ have shown that the compound is probably Fe_2Ti .*

QUASI-BINARY SYSTEM COBALT- Fe_2Ti

In order to determine the nature of the system Cobalt- Fe_2Ti more completely, the three alloys available were examined metallographically after quenching from various temperatures. Although the determination of true precipitate by this method was difficult because of the numerous inclusions, probably titanium oxide and nitride, reasonable data were secured by directing attention to the grain boundaries and assuming that as long as they were clean, no particles of a second phase existed. On this basis concordant data as shown in the diagram of Fig. 2 were derived. Extrapolation of the solidus and solvus† lines indicates a eutectic temperature at about 1200°C . and a maximum solubility of about 25 per cent Fe_2Ti in cobalt.

PRECIPITATION-HARDENING CHARACTERISTICS

From the slope of the solvus line the alloys would be expected to be susceptible to precipitation-hardening. In investigating this phase of the subject the three alloys were quenched after 15 min. at one of three temperatures: 950° , 1150° , and 1300°C ., and then aged for times up to 100 hr. at 600° , 700° , 800° , and 900°C . The diagram in Fig. 2 shows that for the alloys 3124 and 3123 the lowest "solution" treatment did not even approximate complete solution,

*

| | 3125 | 3124 | 3123 |
|------------------------------|------|-------|-------|
| Fe..... | 1.51 | 2.38 | 2.25 |
| Fe_2Ti | 3.79 | 11.90 | 15.62 |

† Solvus line is the line defining the limit of the primary alpha solid solution with respect to temperature and composition; sometimes called the solid solubility curve.

while the highest treatment was just below the solidus. Also, it is evident that for alloy 3125 no hardening would be expected for the two higher "precipitation" treatments, as the alloy would still be in the solid solution condition.

An examination of the data on the three alloys, shown in Fig. 3 with Rockwell B hardness as ordinate plotted against aging time as abscissa, discloses two discordant facts, both in connection with the low ferrotitanium alloy, No. 3125.

1. The higher the solution temperature, the lower is the as-quenched hardness, and the magnitude of this difference (about 28 Rockwell points) is greater than would be anticipated from grain coarsening alone.

2. Appreciable hardening resulted from aging the quenched alloy at 800° and 900°C ., even though, for these temperatures, the alloy falls completely within the solid solution field (Fig. 2). The magnitude of the hardness increase resulting from this varied, being about 20 points for the 1300°C . treatment, about 10 points for that at 1100°C . and only 3 points for that at 950°C .

The first of these effects could be caused either by plastic deformation during quenching or by a partial transformation from the face-centered cubic beta phase, stable at the high temperatures, to the close-packed hexagonal alpha (or epsilon) phase, stable below about 450°C . All the quenched specimens of this alloy show numerous striations (Fig. 10) under the microscope and these could readily be explained by either of the two reasons suggested.

The age-hardening in an apparently uniform solid solution alloy, on the other hand, probably results from the effects of a strain, which might be produced by either of the reasons cited, and thus is similar to the phenomenon of double aging, which has been so extensively studied by R. H. Harrington.⁶ As he points out, "an alloy normally constituted of a single solid solu-

tion phase in the annealed state may be truly precipitation-hardened" by a process of strain-aging in which recrystallization nuclei produce effects similar to those of

LONG-TIME TENSILE DEFORMATION CHARACTERISTICS

For studying the tensile deformation characteristics under dead loading over

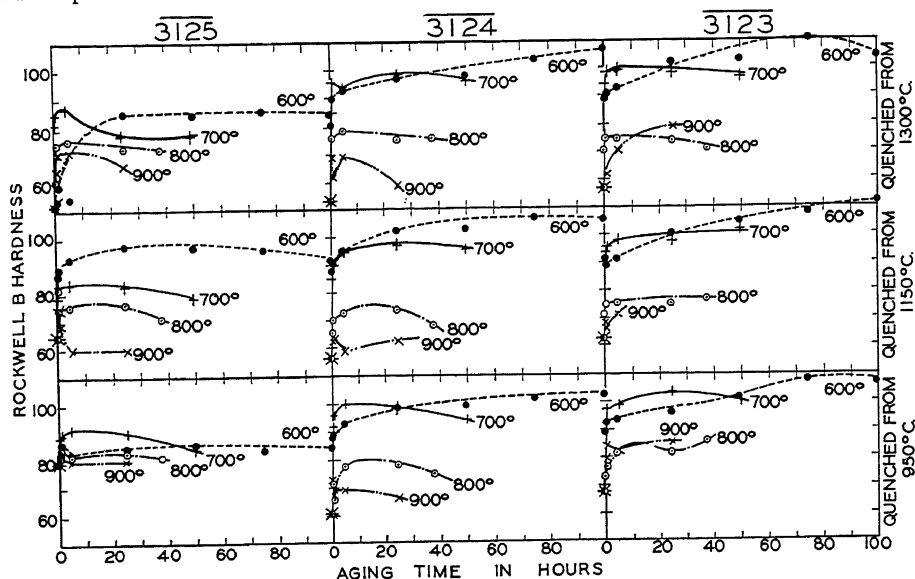


FIG. 3.—CHANGE IN ROCKWELL B HARDNESS WITH TIME OF AGING AT 600°, 700°, 800° AND 900°C. Alloys 3125, 3124, 3123 quenched originally from 1300°, 1150°, and 950°C.

precipitation nuclei in the usual age-hardening processes.

If this strain-aging hypothesis is accepted, it follows that the higher the quenching temperature, the greater the strain induced and the coarser the grain size, and, consequently, the greater the relative effects of strain-aging when reheated. Apparently, the hardening of the fine-grained material quenched from 950°C. is completed during the quench while that of the coarse-grained structures requires subsequent aging for its optimum development. Because of the relatively low solubility of Fe_2Ti in cobalt at 600° and 700°C. it is entirely possible that a large portion of the hardening found on aging at these temperatures is attributable to the same cause, although there are so many effects possible, such as order-disorder changes for example, that definite explanations cannot be given.

periods of several hundred hours, the spring loading furnace, which has already been described in the literature,⁷ was used. This equipment tests a specimen having a gauge length 4 in. long and $\frac{1}{8}$ in. in diameter (Fig. 9). Within the limits of the test, the smallest secondary creep rate that can be determined definitely is 0.01 per cent per 1000 hr., and it will be noted that several of the rates were even less than this. Step loading was used throughout in increments of 2000 lb. per sq. in., a given loading being maintained until the secondary creep rate became essentially constant. This condition generally required upward of 300 hr. The secondary creep rate, so secured, was then designated as the "deformation rate" characteristic of the alloy and the applied stress. Previous work⁷ has indicated that virtually the same secondary creep rates obtain regardless of whether the specimens are step-loaded or loaded throughout the test

with a constant load, always provided, naturally, that the rates remain reasonably low so that the section does not decrease markedly. As a comparative method the test has already proved its worth. However, these creep data are neither presented nor intended for use for purposes of engineering design, but rather as reasonably accurate results of the reactions of these alloys to the specific conditions studied. An additional

before testing in order to obtain an approximately similar structural state. Tests were run at 600°, 700°, and 800°C. and complete data on these tests are compiled in Table 2.

In Fig. 4 the deformation curves for the tests at 600°C. are shown.* Alloy 3125 is the only one that does not show negative creep after the application of the initial load, and this behavior is accounted for by the fact that it is only slightly super-

TABLE 2.—*Tensile Deformation Characteristics at 600°, 700° and 800°C. after Air-quenching from 15 Minutes in Hydrogen at 950°C.*
PERCENTAGE PER 1000 HOURS

| Testing Temperature, Deg. C. | Alloy No. | Fe-Ti, Per Cent | Load, Lb. per Sq. In. | | | | | | | | | | | | | | |
|---------------------------------|-----------|-----------------|-----------------------|---------------------------|------------------|---------------|---------------------------|------------------|---------------|---------------------------|------------------|---------------|---------------------------|------------------|---------------|---------------------------|------------------|
| | | | 2000 | | | 4000 | | | 6000 | | | 8000 | | | 10,000 | | |
| | | | Hours at Load | Cum. Hours at Temperature | Deformation Rate | Hours at Load | Cum. Hours at Temperature | Deformation Rate | Hours at Load | Cum. Hours at Temperature | Deformation Rate | Hours at Load | Cum. Hours at Temperature | Deformation Rate | Hours at Load | Cum. Hours at Temperature | Deformation Rate |
| | | | | | | | | | | | | | | | | | |
| 600 | 3125 | 3.79 | 500 | 500 | <0.01 | 502 | 1002 | <0.01 | 502 | 1504 | 0.03 | 505 | 2009 | 0.05 | 616 | 2625 | 0.03 |
| | 3124 | 11.90 | 500 | 500 | 0.01 | 502 | 1002 | 0.01 | 502 | 1504 | 0.03 | 505 | 2009 | 0.05 | 616 | 2625 | 0.05 |
| | 3123 | 15.62 | 342 | 342 | <0.01 | 328 | 670 | 0.16 | 297 | 967 | 0.22 | 570 | 1537 | 0.31 | | | |
| | 2867 | ? | 500 | 500 | <0.01 | 502 | 1002 | 0.03 | 502 | 1504 | 0.04 | 505 | 2009 | 0.08 | 616 | 2625 | 0.04 |
| 700 | 3125 | 3.79 | 562 | 562 | 0.05 | 1178 | 1740 | 0.35 | 861 | 2601 | 0.90 | 503F | 3104 | 16.04 | | | |
| | 3124 | 11.90 | 562 | 562 | 0.06 | 1178 | 1740 | 0.04 | 861 | 2601 | 0.08 | 579 | 3180 | 0.15 | 569 | 3749 | 0.70 |
| | 3123 | 15.62 | 263 | 263 | 0.53 | 209 | 472 | 0.58 | 209 | 681 | 0.61 | 238 | 919 | 0.88 | | | |
| | 2867 | ? | 562 | 562 | 0.11 | 1178 | 1740 | 0.38 | 861 | 2601 | 0.58 | 579 | 3180 | 1.20 | 569 | 3749 | 2.15 |
| 800 | 3125 | 3.79 | 524 | 524 | 5.75 | 244 | 768 | 16.9 | | | | | | | | | |
| | 3124 | 11.90 | 524 | 524 | 0.63 | 244 | 768 | 3.6 | | | | | | | | | |
| | 3123 | 15.62 | 210 | 210 | 0.43 | 210 | 420 | 1.7 | 209 | 629 | 8.6 | | | | | | |
| | | | | | | | | | | | | | | | | | |

* This value is only an approximation, as the specimen fractured after 503 hr. at 8000 lb. per sq. in. without attaining a constant rate.

alloy, No. 2867, was included in these studies, although, because of insufficient material, it was tested only at 600° and 700°C. As can be seen from its analysis (Ni, 27.0 per cent; Si, 0.71; Fe, 13.55; Ti, 3.45; Mn, 0.28; Co, 54.05; with Al, 0.93 and C, 0.12 also reported), it is similar to alloy 3124 with about 30 per cent of the cobalt in that alloy replaced by nickel and iron. Alloys 3125, 3124 and 2867 were tested at the same time while 3123 was tested earlier and reported erroneously in the literature⁷ as alloy 3124.

All alloys were heated for 15 min. in hydrogen at 950°C. and air-quenched

saturated with ferrotitanium, as indicated in Fig. 2. In general, at this temperature alloy 3123, with the highest ferrotitanium content, seems to be inferior while there is little to choose between the other three.

At the higher temperature of 700°C., the secondary deformation rates were appreciably greater (Fig. 5), and only alloy 2867 showed any negative creep. This was of low magnitude and persisted only during the

* It should be noted that, even though each loading is plotted as starting at zero time, the times at test temperature actually are cumulative, and that this method of plotting was used only to obtain a clearer comparison between the various loadings.

first few hours of test. Deterioration in 3125 with increase of load may also be noted. This would seem to indicate a relatively rapid removal of any hardening

note, too, that, except at the higher loads, the substitution of nickel for cobalt (i.e., 2867 compared with 3124), apparently has not been beneficial.

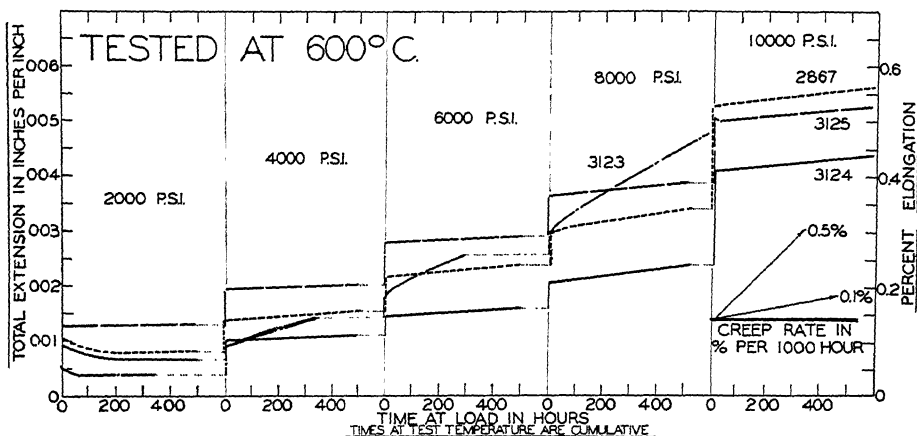


FIG. 4.—DEFORMATION CHARACTERISTICS OF ALLOYS 3125, 3124, 3123 AND 2867 AT 600°C. UNDER SUCCESSIVE LOADS OF 2000, 4000, 6000, 8000 AND 10,000 POUNDS PER SQUARE INCH.

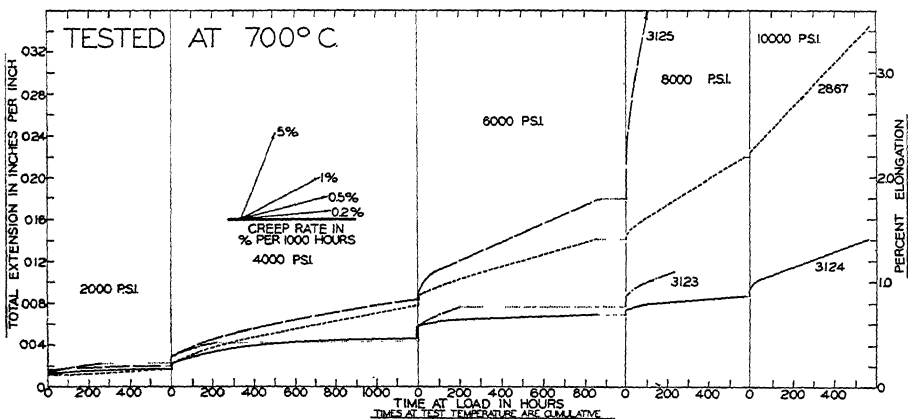


FIG. 5.—DEFORMATION CHARACTERISTICS OF ALLOYS 3125, 3124, 3123 AND 2867 AT 700°C. UNDER SUCCESSIVE LOADS OF 2000, 4000, 6000, 8000 AND 10,000 POUNDS PER SQUARE INCH.

effects resulting either from the small amount of precipitate present or from the strains induced by quenching from 950°C., or by the deformation during the test. The relative weakness of 3123 still persists, and alloy 3124 is clearly the most resistant to deformation at this temperature in spite of the fact that 3123 should have appreciably more precipitate available for strengthening purposes. It is interesting to

The tests at 800°C., the results of which are plotted in Fig. 6, were not extensive. The three Cobalt-Fe₂Ti alloys displayed high deformation rates, and 2867 was not tested because of insufficient material. Resistance to deformation at this temperature appears to be a direct function of iron-titanium additions.

In Fig. 7 the results of the deformation studies are summarized in three plots of the

logarithm of tensile deformation rate (i.e., secondary creep rate), in percentage per 1000 hr., vs. the percentage of Fe_2Ti . This indicates that the higher the test temperature, the greater the amount of Fe_2Ti needed for improved resistance to deformation. There is no clear reason why the high-ferrotitanium alloy should be so much weaker at 600°C. and at 700°C. than the one containing the intermediate amount. At the high temperature it would be expected to be stronger, and the results bear this out. Alloy 3125 also behaves according to expectation since, as Fig. 2 indicates, it would be essentially a solid solution at the two higher temperatures, and consequently would be expected to be weaker. A certain amount of information regarding the deformation can also be secured from Fig. 8, in which stress is plotted against the logarithm of the deformation rate in percentage per 1000 hr. For this method of plotting, the curves for all three alloys at 600°C., and for 3124 and 3123 at 700°C., seem to be very steep near the inflection point. Other

work on deformation in this laboratory has indicated that this shape curve is indicative of work-hardening during the deformation

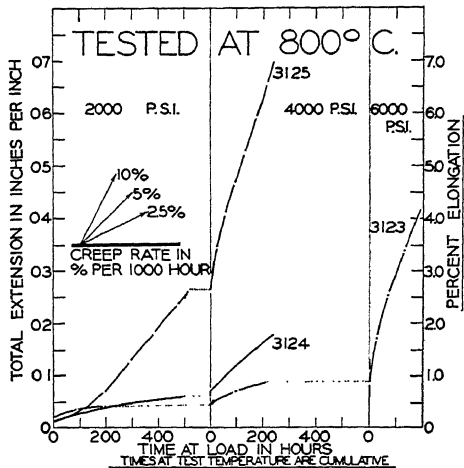


FIG. 6.—DEFORMATION CHARACTERISTICS OF ALLOYS 3125, 3124, AND 3123 AT 800°C. UNDER SUCCESSIVE LOADS OF 2000, 4000, AND 6000 POUNDS PER SQUARE INCH.

test. This would explain then, the weakening of 3125 at 700° and 800°C., since its

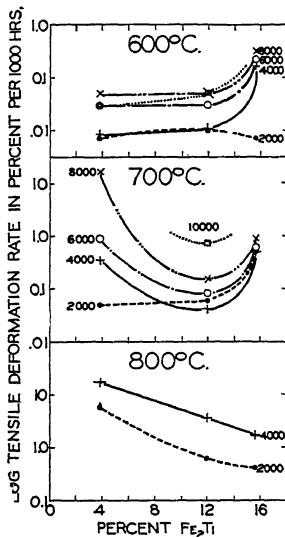


FIG. 7.

FIG. 7.—EFFECTS OF VARYING AMOUNTS OF FERROTITANIUM ON SECONDARY DEFORMATION RATES AT 600°C, 700°C AND 800°C. UNDER LOADS OF 2000 TO 10,000 POUNDS PER SQUARE INCH.

FIG. 8.—VARIATION OF SECONDARY DEFORMATION RATES WITH STRESS FOR ALLOYS 3125, 3124 AND 3123 AT 600°, 700° AND 800°C.

(Curves with a steep inflection region indicate deformation in strain-hardening range.)

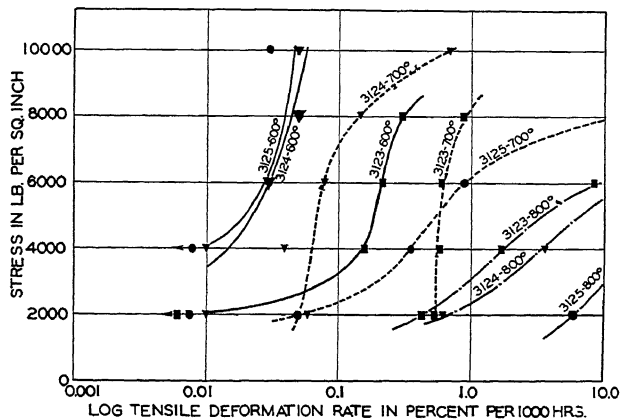


FIG. 8.

"recrystallization" temperature appears to lie between 600° and 700°C.* However, inasmuch as the factors determining the creep rate at which the marked increase

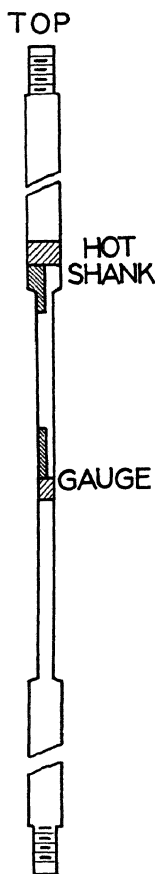


FIG. 9.—TYPICAL DEFORMATION SPECIMEN SHOWING LOCATIONS STUDIED METALLOGRAPHICALLY.

in stress occurs are not as yet known, no definite information can be secured here to explain the apparently anomalous behavior of 3123.

METALLOGRAPHY OF DEFORMATION SPECIMENS

All of the deformation specimens were carefully examined metallographically in

an effort to find correlations between the deformation characteristics and the microstructure. The solution of 60 c.c. hydrochloric, 15 c.c. nitric, and 15 c.c. acetic acids, and 15 c.c. water recommended by Austin and Nickol⁷ was found to be satisfactory for etching, although it was necessary to "age" the reagent before use. This solution was also used for electrolytic etching.

Specimens from both the hot shank and the gauge section were cut as indicated in Fig. 9, so that transverse and longitudinal sections could be examined. In the tests at 800°C. a specimen of some of the materials was held unstressed in the furnace for further comparison.

Figs. 10 to 13 show the appearance of the four alloys after air-quenching from a 15-min. normalizing treatment at 950°C. in hydrogen. All sections show evidence of nonmetallic inclusions, probably titanium oxide and nitride, but the structures appear to be essentially solid solutions. Evidence of a precipitate phase, however, may be noted in the photomicrographs of 3124 and 3123, containing 11.90 and 15.62 per cent Fe_2Ti , respectively (Figs. 11 and 12). In the alloy containing some nickel, a spheroidized phase, which may be the nickel-titanium compound Ni_3Ti (Fig. 13) is distributed. The extremely fine particles appearing at the grain boundaries appear to be similar in type to the precipitate found in alloy 3124 (Fig. 11), although this was not established definitely.

The normalized structures as modified by several hundred hours under stress at 600°C. are shown in Figs. 14 to 17, and are representative of both the gauge and hot-shank portions of the test bar. A fine precipitate has developed in alloys 3125 (Fig. 14) and 3124 (Fig. 15), while in alloy 3123 a marked increase in amount and particle size is evidenced from a comparison in Figs. 12 and 16. The two types of precipitate found in the normalized structure of 2867

* By the term recrystallization temperature, the authors infer the temperature above which

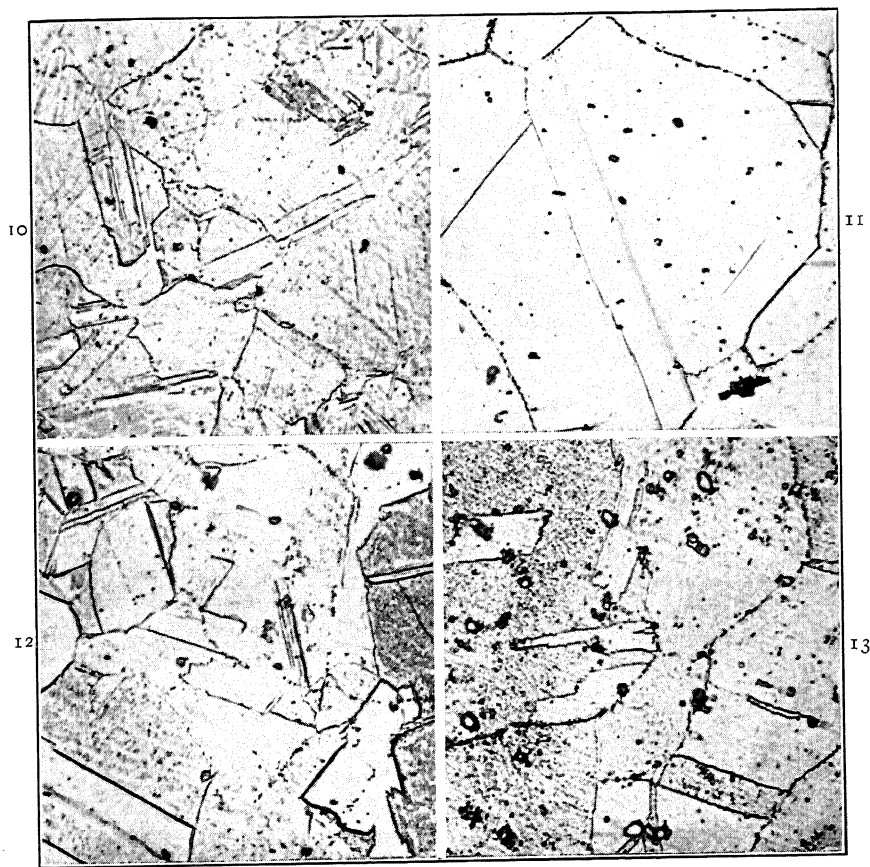
the effects of a given strain do not accumulate but are removed concomitantly.

are much more clearly revealed (Fig. 17) after prolonged testing at 600°C.

With the exception of alloy 2867, little difference, except for the usual coarsening

in a considerable increase in the amount of the fine precipitate.

In raising the test temperature to 800°C. the changes in microstructure of some of



FIGS. 10-13.—EFFECTS OF NORMALIZING TREATMENT OF 15 MINUTES IN HYDROGEN AT 950°C. UPON MICROSTRUCTURES ETCHED IN MIXED ACID SOLUTION. $\times 750$.

Fig. 10. Alloy 3125 (3.79 per cent Fe_3Ti).
 Fig. 11. Alloy 3124 (11.90 per cent Fe_3Ti).
 Fig. 12. Alloy 3123 (15.62 per cent Fe_3Ti).
 Fig. 13. Alloy 2867 (cobalt-nickel- Fe_3Ti).

of precipitate, was observed in the structures obtained after testing at 700°C. as compared with those at 600°C., and no differences could be recorded between the gauge cross sections and those of the hot shanks. However, with alloy 2867 the increase in test temperature from 600° to 700°C. resulted not only in an increase in the size of the spheroidal particles but also

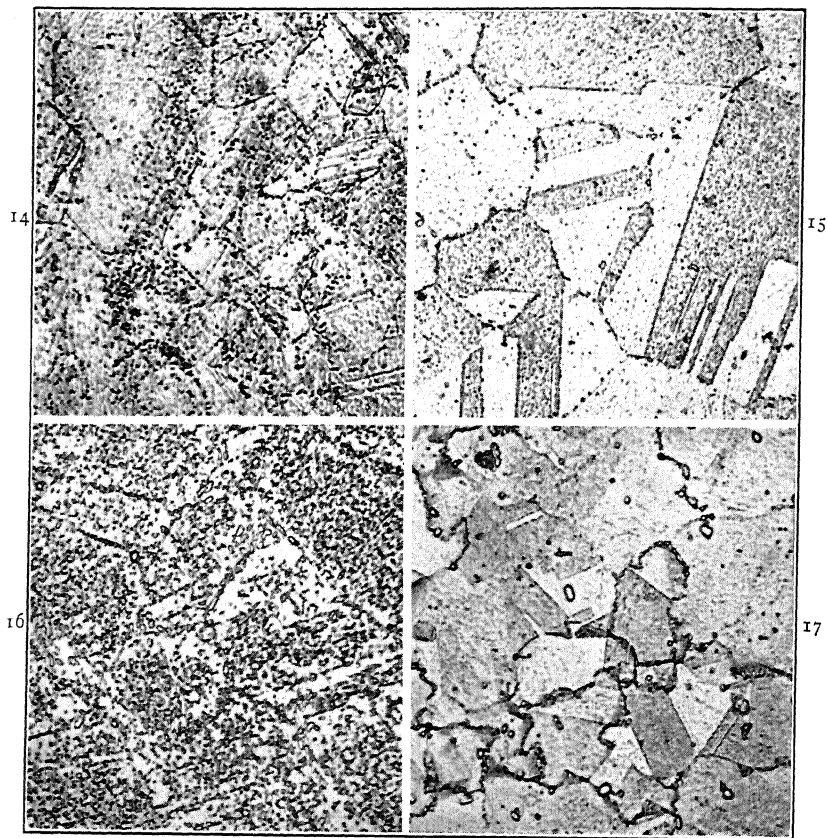
the alloys as well as the differences observed as a result of stress or plastic deformation were much more marked.*

The alloy containing the smallest amount of ferrotitanium addition (3.8 per cent in 3125) showed a structure similar to those

* These facts are brought out more clearly in a direct study of several areas under the microscope.

found after testing at the lower temperatures, whether the section was taken from the gauge length of the test specimen (Fig. 18) or from an unstressed sample

shown. Inasmuch as an examination of the transition section disclosed no sharp demarcation between the structures of the gauge and hot shank, it would seem that



FIGS. 14-17.—EFFECTS OF TESTING AT 600°C. UPON MICROSTRUCTURES. ETCHED IN MIXED ACID SOLUTION. $\times 750$.

Fig. 14. Alloy 3125, transverse gauge section.

Fig. 15. Alloy 3124, transverse gauge section.

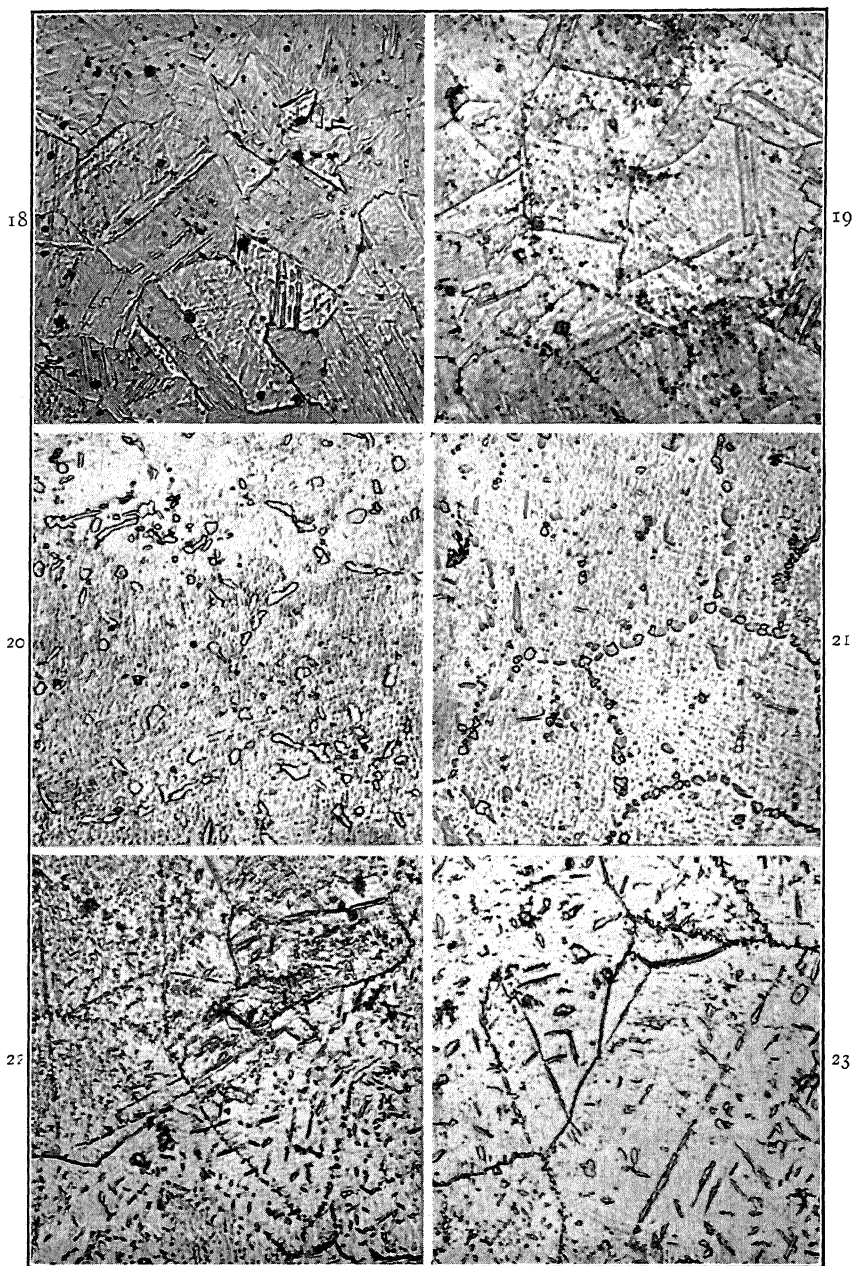
Fig. 16. Alloy 3123, transverse gauge section.

Fig. 17. Alloy 2867, transverse gauge section.

(Fig. 19). Alloy 3124 did show certain differences, however. The gauge structure, shown in Fig. 20, is seen to have large particles of precipitate outlining the grain boundaries. A comparison of this and the unstressed material (Fig. 21) indicates that the particles are somewhat smaller in the latter. The structure of the hot shank was intermediate between the two and is not

the plastic deformation in the gauge length could either have accelerated the agglomeration of the precipitate or produced a more rapid rate of precipitation on a limited number of grain-boundary particles.

The structures of 3123, the gauge of which is illustrated in Fig. 22 and the hot shank in Fig. 23, indicate that here plastic deformation apparently has tended to



FIGS. 18-23.—EFFECTS OF TESTING AT 800°C . UPON MICROSTRUCTURES. ETCHED IN MIXED ACID SOLUTION. $\times 750$.

Fig. 18. Alloy 3125, transverse gauge section.

Fig. 19. Alloy 3125, heated unstressed.

Fig. 20. Alloy 3124, transverse gauge section.

Fig. 21. Alloy 3124, heated unstressed.

Fig. 22. Alloy 3123, transverse hot-shank section.

Fig. 23. Alloy 3123, transverse gauge section.

increase the dispersion rather than the agglomeration of the particles. However, it will be noted that in this specimen the precipitation seems to be general rather than concentrated at grain boundaries as in alloy 3124. Consequently, if the plastic strain served to increase the number of nuclei as well as the rate of precipitation, the structure would give an impression of a decreased degree of dispersion even though a greater amount of precipitation actually had occurred. This may be what actually happened.

A specimen of 2867 held at 800°C. unstressed for a time comparable with those of the other specimens was similar in structure to 3124 except for the presence of the numerous large particles, probably Ni_3Ti , which have been commented upon previously.

SURFACE STABILITY

The four alloys differed noticeably in the character and degree of their surface stability during the test. The three cobalt-ferrotitanium alloys all showed indications of intergranular attack although their resistance seemed to increase with increase in the amount of ferrotitanium. The scale formed was not very adherent. On the other hand, the cobalt-nickel-ferrotitanium alloy expanded somewhat during the test apparently because of a marked penetration of oxygen or nitrogen at the surface, and the alloy was free from selective grain-boundary attack.

CONCLUSIONS

1. The alloys investigated are susceptible to precipitation-hardening.
2. 600°C. is a favorable aging temperature regardless of the solution treatment used.
3. With the 1150° and 1300°C. solution treatments some precipitation-hardening occurs even at temperatures apparently in the solid solution range.

4. Tensile deformation rates at high temperature are affected by the oxidation resistance and by the amount and degree of dispersion of the precipitates.

5. Both 600° and 700°C. appear to be within the strain-hardening temperature range of the two richer alloys for the stresses studied. However, the alloy containing the smallest amount of ferrotitanium strain-hardened only at the lower temperature.

6. Ni_3Ti seems more prone to precipitate discontinuously at the grain boundaries while Fe_2Ti occurs more frequently as a general precipitate within the grains.

7. From microexamination it is concluded that at the higher test temperatures (700° and 800°C.) stress may have accelerated the precipitation reactions.

ACKNOWLEDGMENT

Mr. Robert M. Allen, a graduate student in metallurgy, assisted greatly in certain parts of the metallographic work, and in the heat-treatments employed to establish the quasi-binary diagram.

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DISCUSSION

(C. S. Barrett presiding)

J. TUCKER MACKENZIE,* Kearny, N. J.—In the microstructures of the materials held 2000 to 3000 hr. at 600° to 800°C., there appears to be a similarity between some of the precipitates

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obtained by the authors and various kinds of nitride precipitates, principally iron nitride. Inasmuch as nitrogen is quite soluble in iron at these temperatures, it would seem possible that sufficient nitrogen, from the air atmosphere used, diffused into the alloys and was precipitated as iron nitride particles.

In the 1936 Proceedings of the International Acetylene Congress, Seferian⁸ and Portevin and Seferian⁹ show photomicrographs of various types of iron nitride precipitates. Their work, in addition to recent experience of the discussor, would suggest that the precipitates exhibited in the photomicrographs cited might possibly be a form of iron nitride. In any event, this interesting point should be investigated, in order to ascertain, if possible, the true identity of the precipitates.

As a tool for such an investigation, a modifi-

cation of Fry's etching reagent might be suggested. This reagent, consisting of anhydrous cupric chloride, hydrochloric acid and ethyl alcohol, has been found by the writer to be the most satisfactory reagent for etching iron nitrides.

C. R. AUSTIN AND C. H. SAMANS (authors' reply).—Mr. MacKenzie's comments are very interesting, especially since effects such as those mentioned by him have often been overlooked in the past. In the commercial development of these alloys the possibility of nitrogen penetration certainly must be carefully considered. We, however, have been unable to show that the needlelike structure in our specimens is due to the precipitation of nitrides. The modified Fry's reagent suggested by Mr. MacKenzie seems to etch the structure exactly as did the mixed acid reagent used for the illustrations in the paper; hence we are inclined to believe that the structure is due to a coarse precipitate of an iron-titanium compound rather than to nitrides formed during the long exposure to air at the elevated test temperature.

⁸ D. Seferian: Influence de l'Azote sur la Soudabilité des Aciers (Influence of Nitrogen on Weldability of Steel). *Proc. Int. Acetylene Congress* (1936).

⁹ A. Portevin and D. Seferian: Etude de la Formation des Nitrures Métalliques dans la Soudure des Aciers (Formation of Metallic Nitrides in Welding of Steels). *Proc. Int. Acetylene Congress* (1936).

Effect of Cold-work upon Electrical Conductivity of Copper Alloys

BY D. K. CRAMPTON,* H. L. BURGHOFF,† MEMBERS A.I.M.E., AND J. T. STACY‡

(New York Meeting, February 1941)

THE effect of cold-working upon electrical conductivity of copper and of copper alloys appears not to be generally known in detail. Although several papers on the subject have been presented, showing variable effects according to alloy composition, it is often assumed that the 2 to 3 per cent lowering of the conductivity of ordinary tough-pitch copper by severe cold-working is typical for copper alloys. Because of this situation it was decided to carry out the present work upon several types of copper, copper-zinc alloys over the commercial range of brasses, other binary alloys, and numerous age-hardening alloys in the quenched, and quenched and aged conditions. The large number of alloys investigated made it impossible to study every one in the detail it may have merited. Inasmuch as several interesting points that could not be satisfactorily explained came to light, further work is contemplated by the authors.

It is usually considered that the normal effect of cold-work on ductile metals and unordered alloys is to decrease conductivity slightly. In alloys that are in the ordered state, as annealed or otherwise heat-treated, cold-working tends to disorder the structure, resulting in very marked lowering of conductivity. The random state of atomic arrangement produces lower con-

ductivity than the ordered state for the same composition.¹

PREVIOUS WORK

Previous work in the authors' laboratory has shown the electrical conductivity of several copper alloys to be decreased by greater amounts than might have been expected, in view of the general knowledge on the subject, when cold-worked.

Guillet and Ballay² investigated the influence of cold-work upon the resistivity of several metals and alloys, including copper and some copper alloys. The increase of resistivity due to severe working was less than 4 per cent for all pure metals tested, while the increases for the alloys were generally higher. In the copper-zinc alloys, they found that the increase of resistance due to drawing increased with zinc content, and reported a 21.7 per cent increase of resistance for an alloy containing 67.9 per cent Cu as severely worked.

Masima and Sachs³ studied the change in electrical resistance of three brass crystals when stretched in the tensile test, obtaining increases in resistance of the order of 3 per cent for 30 to 40 per cent reduction of area of the specimens. The resistance decreased again when the cold-worked crystals were subsequently annealed.

Bardenheuer and Schmidt⁴ found that the conductivity of copper was decreased by 3 to 4 per cent when reduced 50 per cent by working. The conductivity of 72-28

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¹ References are at the end of the paper.

brass, rolled 75 per cent, increased 7 per cent when annealed 4 hr. at 200°C. and increased 17 per cent when similarly annealed at 225°C.

Tammann and Dreyer⁵ investigated the recovery of electrical resistance of copper and several binary copper alloys as well as other materials. Their materials were cold-worked 96 to 98 per cent and then heated at increasing temperatures. The decrease in resistance from the cold-worked to the completely recrystallized state was 20.5 per cent for an alloy containing 72 per cent Cu and 28 per cent Zn.

TEST MATERIAL AND PROCEDURE

The alloys for the investigation included four types of copper, several binary alloys of copper with zinc, tin, aluminum, nickel and silicon, respectively, as well as a number of binary and ternary age-hardening copper-base alloys. Electrolytic copper, zinc and nickel were used in the preparation of the alloys and other addition elements were used in as high a degree of purity as was commercially available, in order to have a minimum amount of impurities in the finished alloys. All of the alloys used were analyzed spectrographically for impurities. With few exceptions, total impurities were less than 0.01 per cent. About 0.02 and 0.04 per cent Fe were present in the two copper-silicon alloys of higher silicon content. In the copper-beryllium alloy, 0.08 per cent Al and 0.04 per cent Fe were present. About 0.04 per cent Al and Fe each were present in the copper-zirconium alloy. The copper-cobalt-phosphorus and copper-titanium-silicon alloys contained 0.03 and 0.02 per cent Fe, respectively.

With the exception of the four types of copper, which were taken from commercial sections, the alloys were cast with laboratory high-frequency melting equipment in the form of rods $1\frac{1}{2}$ in. in diameter. These were processed to 0.204-in. dia., on which size they were annealed or otherwise heat-

treated in an automatically controlled electric furnace. A drawing series was then made for each item, yielding material as drawn with reductions of area of 0 per cent and approximately 37, 60 and 84 per cent. The alloys in any one group were processed simultaneously in order to avoid possible variations in test results arising from slight departures from nominally identical treatments.

Alloys of the compositions shown in Tables 1 and 2 were subjected to conductivity tests and, in some cases, tensile tests. Only one sample was available per item for electrical conductivity determination, but check tests were made by reversal of the specimens in the bridge. For all except the high-conductivity coppers, this meant that the actual potential determinations were made in two different parts of each specimen. The tensile tests were made upon the conductivity specimens, two and sometimes three items being tested per condition.

The electrical conductivity tests were made upon a Hoopes conductivity bridge, accurate to a reading of 0.15 per cent. The tensile tests were made upon a new and recently calibrated hydraulic testing machine, using the appropriate range in each case. This machine was accurate to well within 0.5 per cent over the testing range.

The annealing of all material was for periods of 1 hr. unless otherwise indicated. Specimens were air-cooled after annealing, except a few items, which were quenched and are so indicated in the tables and discussions.

DISCUSSION OF RESULTS

Copper

The effect of cold-drawing upon the conductivity of electrolytic tough-pitch copper, high-conductivity Lake copper, oxygen-free high-conductivity copper, and phosphorized copper is shown in Fig. 1. For phosphorized copper (0.029 per cent P) the decrease in conductivity due to working

is almost negligible, being less than 1 per cent as drawn 84 per cent. Oxygen-free high-conductivity and Lake coppers show an almost identical decrease in conduc-

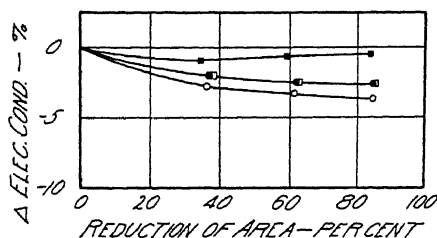


FIG. 1.—CHANGE OF CONDUCTIVITY OF FOUR TYPES OF COPPER AS ANNEALED AND DRAWN.

Open circles, electrolytic tough pitch.

Filled circles, Lake tough pitch.

Open squares, oxygen-free high-conductivity.

Filled squares, phosphorized.

tivity, which is somewhat greater than for the phosphorized copper. Electrolytic tough-pitch copper shows the greatest effect of these four materials, the conductivity having decreased about 3.5 per cent as drawn 84 per cent. The effect of cold-working upon the conductivity of these coppers is small, and in general agreement with values previously reported for copper. There are very definite differences among the materials, as the present results indicate, for reasons which are not apparent.

The percentage change in conductivity referred to for these materials and all others reported here is referred to the original conductivity for each material regardless of its actual value. The change is not to be construed as an arithmetical difference in terms of I.A.C.S.

Copper-zinc

The results for the various tests made upon copper-zinc alloys for zinc contents ranging up to approximately 40 per cent are shown in considerable detail in Figs. 2 to 7, inclusive. It was found (Fig. 2) that the conductivity of each of these alloys decreased regularly as percentage reduction by drawing increased. The corresponding

regular increase of tensile strength is shown in Fig. 3. The change of conductivity due

TABLE I.—Composition and Electrical Conductivity in the Annealed Condition of Work-hardening Alloys Used

| Alloy No. | Composition | Temperature of Anneal, Deg. C. | Electrical Conductivity Annealed, Per Cent I.A.C.S. | |
|-----------|---------------------------------|--------------------------------|---|--|
| COPPERS | | | | |
| 1 | Electrolytic Tough Pitch | 525 | 102.1 | |
| 2 | Oxygen Free High Conductivity | 525 | 101.4 | |
| 3 | Phosphorus Deoxidized—0.029 % P | 525 | 83.9 | |
| 4 | Tough Pitch Lake—0.015 % Ag | 525 | 100.5 | |
| ALLOYS | | | | |
| Alloy No. | Cu, Per Cent | Alloying Elements, Per Cent | Temperature of Anneal, Deg. C. | Electrical Conductivity Annealed, I.A.C.S. |
| 51 | 89.65 | 10.35 Zn | 525 | 43.8 |
| 52 | 84.70 | 15.30 Zn | 525 | 30.9 |
| 53 | 79.61 | 20.39 Zn | 525 | 32.0 |
| 54 | 74.18 | 25.82 Zn | 525 | 30.1 |
| 55 | 69.63 | 30.37 Zn | 525 | 28.5 |
| 56 | 64.63 | 35.37 Zn | 525 | 27.1 |
| 57 | 60.17 | 39.83 Zn | 525 | 28.8 |
| 7 | 74.44 | 25.56 Zn | 525 | 30.0 |
| 41 | 70.00 | 30.00 Zn | 700 | 30.1 |
| | | | 900 Q ^a | 27.9 |
| | | | 900 | 28.4 |
| 39 | 59.78 | 40.22 Zn | 900 FC ^a | 28.5 |
| | | | 425 Q ^a | 29.3 |
| | | | 525 Q ^a | 29.1 |
| | | | 700 Q ^a | 30.3 |
| 9 | 97.40 | 2.44 Sn | 525 | 32.1 |
| 11 | 91.15 | 8.68 Sn | 525 | 13.5 |
| 12 | 97.52 | 2.49 Al | 525 | 24.3 |
| 13 | 94.97 | 4.99 Al | 525 | 17.8 |
| 14 | 92.53 | 7.50 Al | 525 | 15.9 |
| | | | 900 Q ^a | 16.1 |
| | | | 1010 Q ^a | 15.9 |
| 15 | 89.48 | 10.08 Ni, 0.49 Mn | 700 | 11.1 |
| 16 | 79.53 | 20.02 Ni, 0.46 Mn | 700 | 6.5 |
| 17 | 75.82 | 23.38 Ni, 0.48 Mn | 700 | 5.7 |
| 18 | 70.24 | 29.11 Ni, 0.50 Mn | 700 | 4.7 |
| 19 | 99.01 | 0.95 Si | 600 | 18.4 |
| 20 | 97.95 | 1.95 Si | 600 | 10.5 |
| 21 | 96.79 | 2.99 Si | 600 | 8.0 |

^a Q, water-quenched; FC, furnace-cooled. Where no qualifying symbol is given, alloys were air-cooled.

to drawing increased with zinc content to 25 to 35 per cent Zn, after which the effect

for the higher zinc alpha alloys became less (Fig. 4a). As drawn 37 per cent, 61 per cent and 84 per cent, the maximum effects were at about 25.8 per cent Zn (approximately Cu_3Zn), 30 per cent Zn and 35 per cent Zn, respectively. The alloy containing

is at least qualitatively related to the effect upon tensile strength as seen by comparison of Fig. 4a, showing conductivity change as a function of zinc content, and Fig. 4b, which shows tensile-strength change (lb. per sq. in.) as a function of zinc con-

TABLE 2.—*Composition and Initial Electrical Conductivity of Age-hardening Alloys Used*

| Alloy No. | Composition, Per Cent | | Temperature of Quench, Deg. C. | Aging Treatment | | Electrical Conductivity as Heat-treated, Per Cent I.A.C.S. |
|-----------|-----------------------|------------------|--------------------------------|-----------------|----------------------|--|
| | Cu | Other Elements | | Time, Hr. | Temperature, Deg. C. | |
| 22 | 98.78 | 1.24 Cd | 600 | 4 | 250 | 88.5 |
| | | | 600 | | | 88.2 |
| 23 | 97.10 | 2.65 Fe | 1030 | 8 | 650 | 21.0 |
| | | | 1030 | | | 40.9 |
| 26 | 98.12 | 1.89 Ti | 900 | 4 | 500 | 8.0 |
| | | | 900 | | | 18.2 |
| 27 | 98.35 | 1.53 Be | 800 | 24 | 350 | 21.2 |
| | | | 800 | | | 31.6 |
| 28 | 99.21 | 0.53 Zr | 800 | 8 | 450 | 61.5 |
| | | | 800 | | | 78.3 |
| 30 | 98.93 | 0.76 Fe, 0.24 P | 900 | 4 | 450 | 36.5 |
| | | | 900 | | | 69.1 |
| 32 | 98.79 | 0.87 Co, 0.16 P | 900 | 4 | 450 | 34.1 |
| | | | 900 | | | 51.7 |
| 35 | 96.33 | 2.92 Ni, 0.69 Si | 900 | 4 | 450 | 17.7 |
| | | | 900 | | | 32.2 |
| 36 | 99.27 | 0.43 Ti, 0.22 Si | 900 | 8 | 650 | 32.8 |
| | | | 900 | | | 55.5 |
| 25 | 97.03 | 2.85 Co | 950 | 1 | 600 | 17.2 |
| | | | 950 | 2 | 600 | 37.5 |
| | | | 950 | 8 | 600 | 38.6 |
| | | | 950 | 8 | 600 | 39.3 |
| 29 | 98.49 | 1.17 Ni, 0.24 P | 800 | 1 | 400 | 30.3 |
| | | | 800 | | | 46.0 |
| | | | 800 | 3 | 400 | 53.8 |
| | | | 800 | 8 | 400 | 58.7 |
| | | | 800 | 1 | 500 | 59.0 |
| | | | 800 | 3 | 500 | 61.3 |
| | | | 800 | 8 | 500 | 62.9 |
| | | | 800 | 1 | 400 | 30.7 |
| | | | 950 | | | 48.1 |
| | | | 950 | 3 | 400 | 54.7 |
| | | | 950 | 8 | 400 | 58.8 |
| | | | 950 | 1 | 500 | 59.1 |
| | | | 950 | 3 | 500 | 61.2 |
| | | | 950 | 8 | 500 | 63.1 |
| | | | 950 | 1 | 400 | 30.3 |
| | | | 950 | | | 46.0 |

approximately 40 per cent Zn showed appreciable changes in conductivity when drawn, which appeared to vary with respect to the adjacent alpha alloys. This effect is probably due to difference in strain-hardening, as will be seen in the later consideration of strain-hardening characteristics of the group of alloys.

The effect of working upon conductivity

tent. These two groups of curves have similar characteristics, as there is little change between 0 and 10 per cent Zn, followed by more abrupt changes between 10 and 20 per cent Zn, and relatively less change thereafter.

Just as the conductivity and strengthening effects change sharply between 10 and 20 per cent Zn, it is to be remembered that

other properties of copper-zinc alloys, such as color, corrosion resistance with particular regard to the dezincification type of corrosion, and liability to stress corrosion

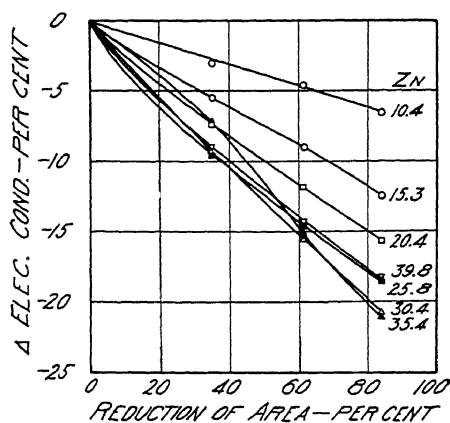


FIG. 2.—CHANGE OF CONDUCTIVITY OF COPPER-ZINC ALLOYS AS ANNEALED AND DRAWN.

failure or season cracking, also change rapidly in this range of composition.

As annealed at 525°C. before drawing, the maximum tensile strength of the alpha copper-zinc alloys occurred at 25.8 per cent Zn, a feature that is clearly shown in Fig. 3. This is partly due to a grain-size effect, for grain size for this anneal increased with zinc content. The 40 per cent Zn alloy was naturally strongest of all at this point, however, because of the presence of beta. The relative tensile strengths of the alpha alloys are not essentially changed when drawn 37 per cent, 61 per cent and 84 per cent, and the 25.8 per cent Zn alloy always has maximum strength. The definitely lower rate of hardening of the 40 per cent Zn alloy in drawing as compared with the high-zinc alpha alloys is evident, for the 40 per cent Zn alloy, which initially was strongest of all, constantly lost rank and finally had the same strength as the 35 per cent Zn alloy at 84 per cent reduction.

Figs. 4*b* and 4*c* show that, although the actual increase in tensile strength (lb. per sq. in.) increased smoothly to a maximum value as zinc content increased and then

decreased slightly in the alpha range, the percentage increase in strength as a function of zinc content was quite different. The curves in the latter case proceed to maxima at about 15 to 20 per cent Zn, then to minima at 25.8 per cent Zn, to maxima again at 30 to 35 per cent Zn, followed by definite decrease again for higher zinc contents, particularly 40 per cent Zn. These effects show the variation in strain-hardening according to zinc content and appear to be quite real.

The strength and strain-hardening characteristics of the 25.8 per cent Zn alloy are distinctive and suggest it to be a critical composition. It corresponds, of course, to a 3:1 copper-zinc atomic ratio. In addition, the large decrease of conductivity of these copper-zinc alloys naturally suggests the possibility of the existence of ordered structure. The present results neither prove nor disprove this possibility. Conductivity changes due to work are indeed profound, as would be expected if ordering were present. Although there is no definite evidence for Cu₃Zn ordered structure, the maximum effect upon conductivity for the group when drawn 37 per cent is found at this composition. The fact that the maximum effect appears to move to alloys of higher zinc content for greater degrees of working may be directly associated with the greater rate of strain-hardening for the higher-zinc alpha alloys.

Although the existence of ordered structure has been established in the beta range of copper-zinc alloys,⁶ there has been little suggestion of an ordered structure corresponding to Cu₃Zn. Based upon a study of 70-30 brass, Wilson⁷ has suggested the possibility of such an ordered structure at high pressure.

Experiments in addition to those made on material annealed at 525°C. and drawn were also made. The effect of annealing temperature on the Cu₃Zn composition was thus studied by making an additional

anneal at 700°C., followed by the same drawing series as used for the other items. No essential difference in effect of working upon conductivity was observed for this

containing approximately 40 per cent Zn was available for this purpose. This alloy was annealed at 425° and 525°C., temperatures just below and just above the β - β'

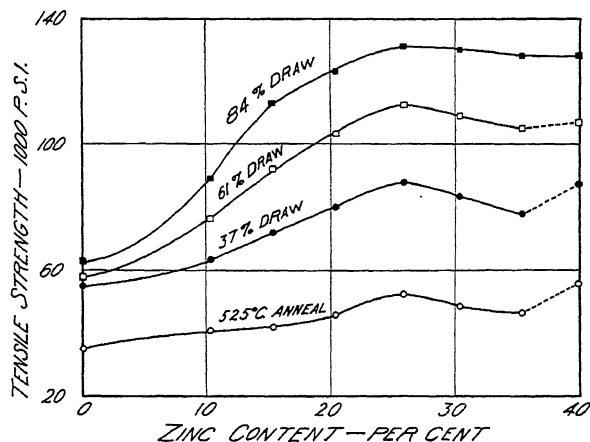


FIG. 3.—TENSILE STRENGTH OF COPPER-ZINC ALLOYS AS ANNEALED AND DRAWN.

anneal. To determine the existence of a possible critical point of ordering as well as effect of manner of cooling from the annealing temperature, a study was made by annealing 70-30 Cu-Zn for 1 hr. at 900°C., followed by quenching, air-cooling and furnace-cooling. The electrical conductivity for all these three treatments was essentially the same as for the 525°C. anneal. There were, however, very slight differences, probably due to cooling strains, for the quenched material had slightly lower conductivity than the others. This small effect disappeared in the drawn tempers. The effect of drawing upon conductivity was naturally similar to that for material annealed at 525°C. Assuming that the quenching operation actually retained the structure formed at high temperature, it would appear, therefore, that the critical point of ordering, if any, does not lie below 900°C., a temperature that is not far from the melting point of the material.

The effect of beta in alpha + beta alloys was investigated in further detail than has already been discussed. A second alloy

transformation, and 700°C., quenched and drawn. The temperature for the β - β' transformation is the critical temperature of ordering.⁶ The conductivity for all treatments was considerably affected by drawing (Fig. 5). The 35 per cent draw showed the same effect for both 425° and 525°C. anneals, but for 60 and 84 per cent draws the change in conductivity for the material annealed at 525°C. became increasingly greater than for that annealed at 425°C. As annealed at 700°C. and drawn, the lowering of conductivity was definitely and increasingly greater for the 35, 60, and 84 per cent draws. Conductivity in this last case was lowered 27.5 per cent when drawn 84 per cent. The hardening effects due to drawing this alloy in all conditions were similar, so that the effects upon conductivity appeared to be due to the increasing amount of beta and not to any differences in strain-hardening. Probably there were no differences in the characteristics of the beta as quenched from the various temperatures. Sykes and Wilkinson,⁶ as well as others, have concluded

that the β - β' transformation in brass is not appreciably retarded by quenching.

The effect of annealing the copper-zinc wires as drawn 84 per cent was investigated

above. Fig. 6 shows that the conductivity for any alloy in this annealing series increased continuously but not lineally, as the annealing temperature increased. The

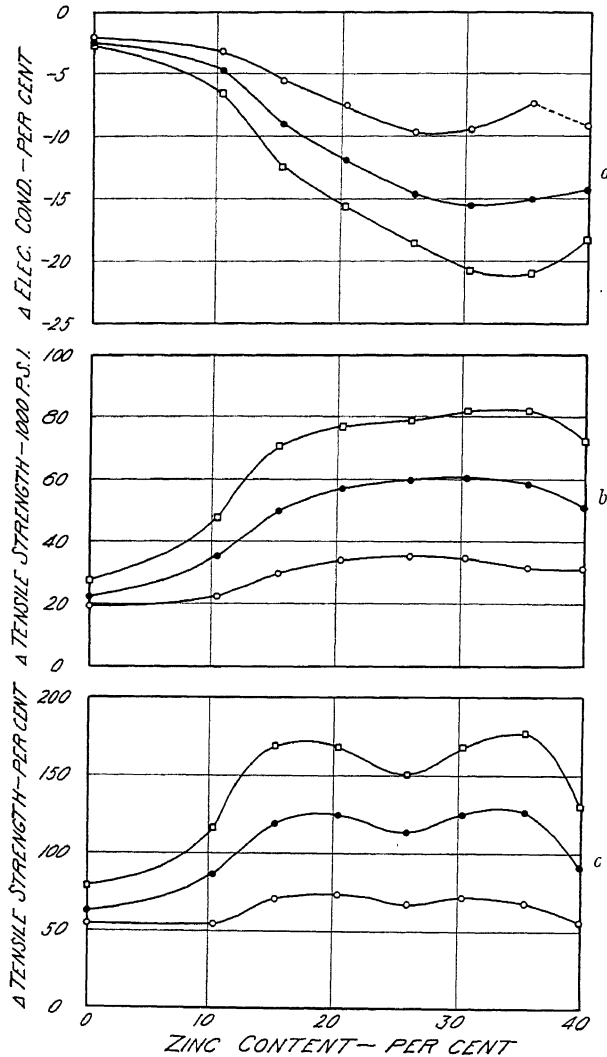


FIG. 4 —CHANGE IN CONDUCTIVITY AND TENSILE STRENGTH OF COPPER-ZINC ALLOYS AS ANNEALED AND DRAWN.

Open circles, 37 per cent draw.

Filled circles, 61 per cent draw.

Square, 84 per cent draw.

from 100°C. through the recrystallization range and finally at 525°C. This material was from the drawing series discussed

effect was noticed even for the anneal at 100°C., for all alloys except the one containing 25.8 per cent Zn. The slope of

these curves, which show the increase of conductivity as a function of annealing temperature, increases as annealing temperature first increases, then decreases somewhat during the so-called relief-annealing range for most alloys, increases sharply in the recrystallization range, and then changes but little to the 525°C. anneal. The 40 per cent Zn alloy was an exception in the annealing series. The conductivity of this alloy rose to a maximum value at 280° and 300°C., a value higher than for the original 525°C. anneal, and decreased again for anneals at 425° and 525°C. This effect was checked by results for other material of similar composition and appeared to be real, although the reason for the effect has not yet been determined. For all the copper-zinc alloys there is considerable increase in conductivity in the relief-annealing range, so that it is possible to have improved combinations of strength and conductivity as compared with the as-drawn condition.

There appeared to be nothing critical at 25.8 per cent Zn in this anneal except extremely vaguely for the lowest temperatures, 100°, 160° and 180°C., where less

With regard to changes of tensile strength in the annealing series (Fig. 7), there appears to be a recovery or softening effect for 10 and 15 per cent Zn as anneal-

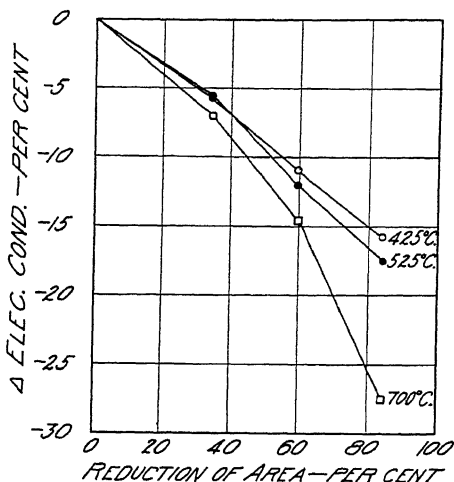


FIG. 5.—CHANGE IN CONDUCTIVITY OF COPPER-ZINC ALLOY CONTAINING 39.8 PER CENT ZINC (ALPHA + BETA STRUCTURE) AS ANNEALED AND QUENCHED AT 425°C., 525°C., AND 700°C. AND DRAWN.

ing temperature increases to 180° and 200°C., respectively, after which there is

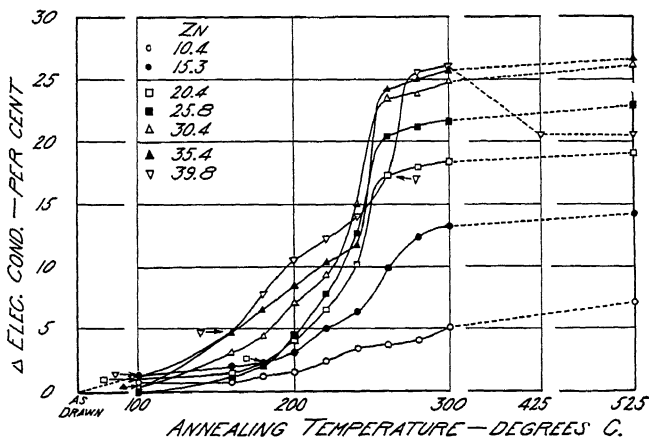


FIG. 6.—CHANGES IN CONDUCTIVITY OF COPPER-ZINC ALLOYS, PREVIOUSLY DRAWN 84 PER CENT, AS ANNEALED FOR ONE HOUR AT TEMPERATURES INDICATED.

change was wrought in the conductivity of this alloy than for neighboring compositions.

a slight hardening effect before recrystallization and softening, although the tensile strength does not quite attain the value

as drawn. This apparent superposition of hardening upon recovery effects may conceivably be due to incipient nucleation, in which submicroscopic nuclei serve to pro-

6500, 7000, 11000 and 5500 lb. per sq. in. for the alloys containing approximately 20, 25, 30, 35, and 40 per cent Zn, respectively, and are more or less in line with the losses

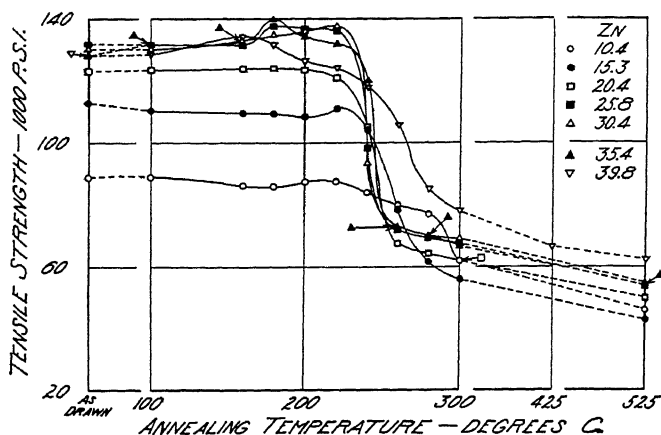


FIG. 7.—TENSILE STRENGTH OF COPPER-ZINC ALLOYS, PREVIOUSLY DRAWN 84 PER CENT, AS ANNEALED FOR ONE HOUR AT TEMPERATURES INDICATED.

duce a precipitation-hardening effect. For the higher zinc contents, there are definite

of conductivity suffered by these alloys when drawn 84 per cent. There is no quantitative relation between increase of conductivity and increase of tensile strength in this low-temperature annealing range.

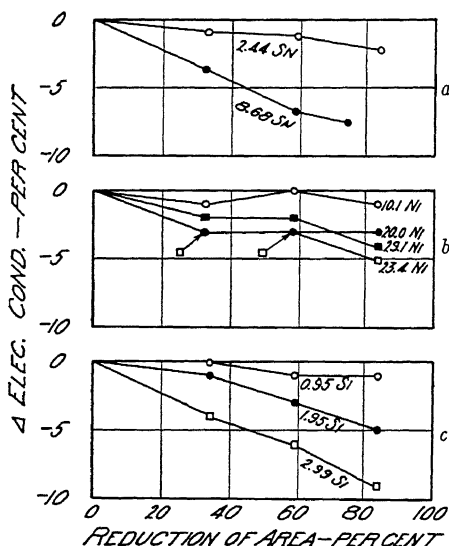


FIG. 8.—CHANGE IN CONDUCTIVITY OF COPPER-TIN, COPPER-NICKEL AND COPPER-SILICON ALLOYS AS ANNEALED AND DRAWN.

increases in strength prior to softening and recrystallization, which amount to 1000,

Copper-tin

Two copper-tin alloys were tested with results as shown in Fig. 8a. The conductivity of the alloy containing 2.44 per cent Sn decreased 2.2 per cent as drawn 84 per cent, an effect of the same magnitude as shown by the coppers. The alloy containing 8.68 per cent Sn showed greater effect, the conductivity decreasing 7.5 per cent as drawn only 74 per cent.

Copper-nickel

Four copper-nickel alloys ranging from 10 to 29 per cent Ni were tested and results are shown in Fig. 8b. Each alloy contained approximately 0.5 per cent Mn as deoxidizer. Although these alloys showed consistent trends with regard to conductivity decrease due to drawing, the conductivity

ity changes for these high-resistance copper-nickel alloys are of about the same order as the accuracy of the measurement of conductivity. The decrease of conductivity is not great in any case and appears to be entirely a normal work-hardening effect. There is no evidence of ordered structure for the alloy containing 23.4 per cent Ni, although the copper and nickel in this alloy are in such ratio as to permit Cu_3Ni arrangement.

Copper-silicon

Copper-silicon alloys containing 0.95, 1.95 and 2.99 per cent Si showed conductivity decreases of 1 per cent, 5 per cent and 9 per cent, respectively, as drawn 84 per cent. The results are shown in Fig. 8c. The trends in the group were consistent and conductivity decreased as percentage of silicon increased and as reduction by drawing increased.

Copper-aluminum

Fig. 9 shows the results obtained on three copper-aluminum alloys containing 2.49, 4.99 and 7.50 per cent Al. Drawing was found to have very great effect on conductivity, the results being comparable to those for the copper-zinc system. The alloy containing 7.50 per cent Al decreased in conductivity by 27.5 per cent when drawn 75 per cent, an amount suggestive of some factor other than simple lattice distortion. This alloy is a composition within the range considered suitable for ordering in accordance with the theory of Easthope as quoted by Nix and Shockley.¹ As the possibility of some kind of ordering in these alloys was thus suggested, the 7.5 per cent Al alloy was additionally annealed at both 900° and 1010°C., quenched and drawn as before. The conductivity results were essentially the same as for the material annealed at 525°C. and drawn. The temperature 1010°C. is just below the melting point for this composition, al-

though theoretically in the $\alpha + \beta$ field, while 900°C. is definitely in the α field. These results indicate that, if

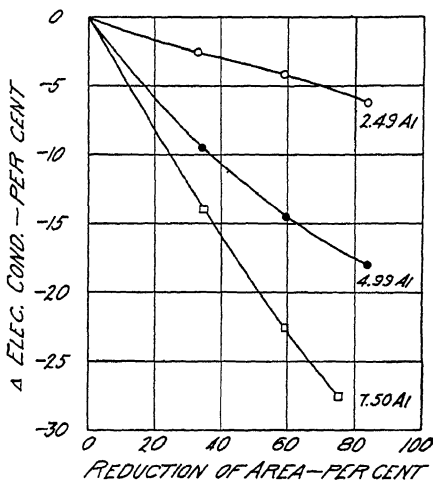


FIG. 9.—CHANGE IN CONDUCTIVITY OF COPPER-ALUMINUM ALLOYS AS ANNEALED AND DRAWN.

ordering is present, there is no critical point of ordering below 1010°C.

Age-hardening Alloys

A number of age-hardening alloy systems were investigated, a typical composition for each system being selected. In most cases one quenching and one aging treatment were used, which were suited to the particular composition.

It was observed that the curves for the change in electrical conductivity as a function of reduction of area by drawing after a solution treatment followed three general patterns. In the first group there was a more or less regular decrease in conductivity with increasing draw. The second group was characterized by increased conductivity for lower degrees of reduction, followed by a decrease for the higher reductions. In the third group, the lighter draws resulted in reduction of conductivity, while more severe reductions lowered conductivity less or even caused an actual increase.

The first case, for which conductivity decreases regularly with degree of cold-working, is an example of the normal effect shown above for copper and its alpha

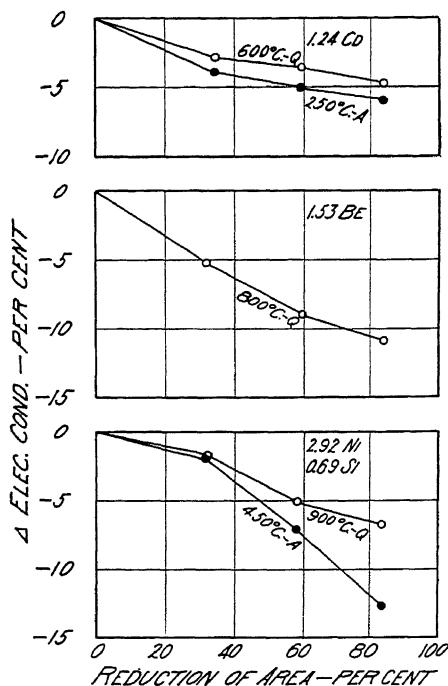


FIG. 10.—CHANGE IN CONDUCTIVITY OF COPPER-CADMIUM, COPPER-BERYLLIUM AND COPPER-NICKEL-SILICON ALLOYS AS HEAT-TREATED AND DRAWN.

alloys and requires no further comment at this point. In the second case, the initial rise of conductivity may be explained by a precipitation from the supersaturated solution induced during the cold-working. The ensuing decrease of conductivity is due to the predominance of the normal effect of cold-working. The third case is in reality similar to the second and the rise in conductivity for the higher degrees of reduction may be due to a belated precipitation effect in working. There is, of course, no assurance that this rise in conductivity would be continued by further working. It is probable that for very extreme degrees of working, the normal effect of working would again predominate.

In the group characterized by a regular decrease in conductivity with increased working of quenched materials are Cu-Cd, Cu-Be, Cu-Ni-Si, and Cu-Co (Figs. 10 and 11). Copper-cadmium alloys decreased regularly with drawing for both as-quenched and as-quenched and aged conditions, the effect being slightly greater than for copper. There were substantially no differences in properties of the alloy for either heat-treatment, which apparently is to be expected from the nature of the system.⁸

The conductivity of the quenched copper-beryllium alloy was decreased by 11 per cent when drawn 84 per cent. When the alloy was aged for 24 hr. at 350°C. it was rendered too hard for drawing, and hence no results are available for such treatment.

The conductivity of the copper-nickel-silicon alloy for both heat-treatments decreased regularly when drawn, showing maximum changes of 6.8 and 12.7 per cent for the quenched and the aged conditions, respectively, as drawn 84 per cent.

The characteristic of the second group is that the conductivity of quenched material first rises and then decreases with increasing severity of draw. Copper-iron, copper-iron-phosphorus and copper-titanium-silicon fell in this group (Fig. 12). The maximum increase in conductivity with the iron alloy was found to be 1.9 per cent at 35 per cent reduction, that for Cu-Fe-P, 1.4 per cent at 59 per cent reduction, and that for the Cu-Ti-Si alloy 3.7 per cent at 37 per cent reduction. With 84 per cent reduction by drawing, the reduction in conductivity for these three alloys was found to be 9.5, 0.8 and 6.1 per cent, respectively. For all three materials as aged, the reduction in conductivity with increasing draw was fairly regular, the maximum reductions with 85 per cent reduction being 2.4, 11.4 and 2.5 per cent for the three alloys, respectively.

In the group characterized by an initial reduction in conductivity when drawn from the quenched condition followed by

an upturn in the curve with more severe reduction, we find copper-zirconium, copper-titanium, copper-cobalt-phosphorus and copper-nickel-phosphorus. The magni-

material when drawn, and the actual decrease bore some relation to the aging time, for the effect upon conductivity became generally less as aging time in-

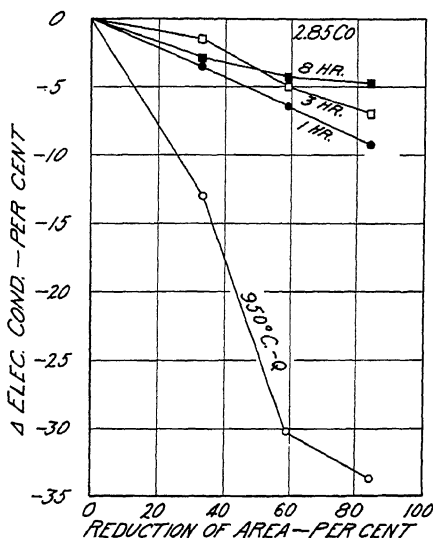


FIG. 11.—CHANGE IN CONDUCTIVITY OF COPPER-COBALT ALLOY AS HEAT-TREATED AND DRAWN.

tude of these effects is obvious from Figs. 13 and 14. The curves for the material drawn after aging appear to be quite normal and appear to need no particular comment.

The copper-cobalt and copper-nickel-phosphorus systems were studied in greater detail with regard to aging conditions. In Fig. 11 the results for the copper-cobalt alloy are shown. Attention is called to the magnitude of the effect when drawing this alloy from the quenched condition. A reduction in conductivity of 33.7 per cent was found for a drawing reduction of 84 per cent. This is the largest proportionate change found in any of the alloys studied. Such an unusual change is not to be expected in such a dilute alloy where the possibility of ordering according to the ordinary conception is remote.

Conductivity of the aged material decreased regularly although to a much smaller extent than for the quenched

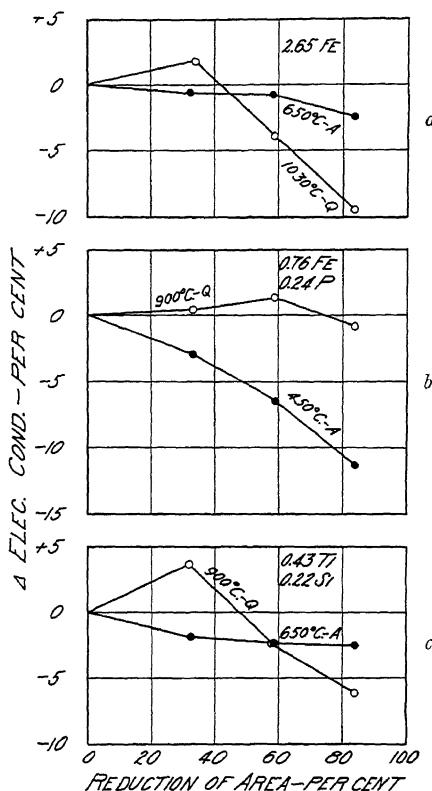


FIG. 12.—CHANGE IN CONDUCTIVITY OF COPPER-IRON, COPPER-IRON-PHOSPHORUS AND COPPER-TITANIUM-SILICON ALLOYS AS HEAT-TREATED AND DRAWN.

creased. The conductivity effect would therefore seem to be dependent upon degree of precipitation, as well as actual degree of strain-hardening.

The copper-nickel-phosphorus alloy was quenched from 800° and 950°C. and aged at 400° and 500°C. for periods of 1, 3 and 8 hr. As mentioned before, the conductivity of the material as quenched from 800°C. decreased very slightly when drawn by amounts up to 60 per cent, then increased by 2.5 per cent when drawn 84 per cent.

When aged at 400°C. after quenching from 800°C., the conductivity decreased regularly in drawing, the decrease becoming less as the aging time increased. When

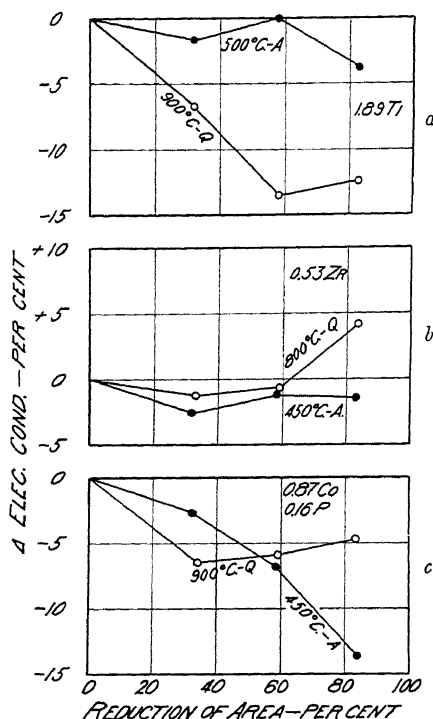


FIG. 13.—CHANGE IN CONDUCTIVITY OF COPPER-TITANIUM, COPPER-ZIRCONIUM AND COPPER-COBALT-PHOSPHORUS ALLOYS AS HEAT-TREATED AND DRAWN.

aged at 500°C. and drawn, similar effects were obtained and the conductivity decrease due to drawing became less as the aging time increased. This group aged at 500°C. showed somewhat less effect due to drawing than did the group aged at 400°C. The results for the alloy as quenched from 950°C, aged and drawn, were similar to those discussed above although the trends were not quite so well defined. These effects may all be associated with the degree of precipitation, for the effect of drawing upon conductivity appears to become less as the degree of precipitation increases.

SUMMARY AND CONCLUSIONS

The effect of cold-working upon the electrical conductivity of several types of copper and of numerous copper alloys has

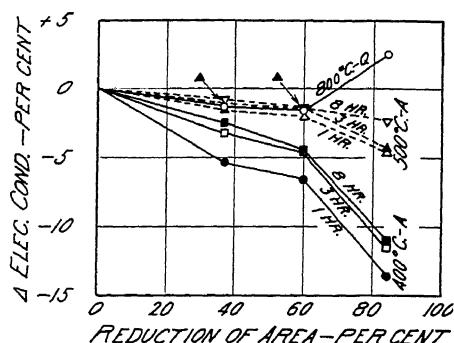


FIG. 14.—CHANGE IN CONDUCTIVITY OF COPPER-NICKEL-PHOSPHORUS ALLOY AS HEAT-TREATED AND DRAWN.

been determined for reductions of area by drawing up to about 84 per cent.

The lowering of conductivity of copper by such working was found to be in general agreement with previously reported results and was less than 4 per cent for reduction of area up to 84 per cent. Slight differences were found among the several commercial types of copper tested, and may be due to presence or absence of oxygen, silver or phosphorus.

For copper alloys of the solid solution or work-hardening type, the results ranged from changes comparable with those for copper to far greater changes, according to composition and degree of working. In general, it was found that the lowering of conductivity increased with alloy content and with degree of draw. Very marked changes occurred in copper-zinc and copper-aluminum alloys.

In the alpha range of copper-zinc alloys, the effect of cold-work upon conductivity increased greatly for alloys containing more than 10 per cent Zn, reaching a maximum in the range 25 to 35 per cent Zn, depending upon degree of working, and thereafter decreasing. An alloy containing 25.8 per cent Zn appeared to be critical and the

large conductivity effects over a wide range of zinc content may possibly have been due to ordered structure corresponding to Cu_3Zn , a composition which this alloy very closely approximated.

The copper-zinc alloys as drawn 84 per cent showed continual recovery of conductivity when annealed for periods of 1 hr. at temperatures ranging from 100°C . and upward through the recrystallization range, the most rapid changes occurring during recrystallization.

In the $\alpha + \beta$ range of copper-zinc alloys, the lowering of conductivity by working was also great and became more pronounced as the proportion of β increased. The existence of ordered structure corresponding to CuZn has previously been demonstrated and probably this accounts for much of the effect found in the $\alpha + \beta$ range.

The conductivity of several age-hardening alloys in the quenched or solution-treated condition was found to be increased for some degrees of drawing, apparently because of precipitation from the supersaturated solution in drawing, although the normal lowering effect predominated for other degrees of draw. Other alloys did not yield such variable results. In the age-hardened state, the decrease of conductivity was roughly proportional to the degree of draw. This is in accordance with the results obtained upon simple work-hardening alloys, which were at no time supersaturated. The degree of saturation of the aged alloys was certainly much less than for the quenched alloys. The magnitude of the effect was also dependent upon the degree of precipitation, for the change became less as aging time increased and also as aging temperature increased.

ACKNOWLEDGMENTS

The authors wish to make due acknowledgment to Messrs. E. L. Smith and P. A. Leichtle for the necessary chemical and spectrographic analyses, and to Mr. H. F.

Schissler for assistance in the preparation of the alloys. Thanks are also due to the Chase Brass and Copper Co. for permission to publish the test results.

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DISCUSSION

(E. E. Schumacher presiding)

W. C. ELLIS,* New York, N. Y.—The authors have presented in one paper a collection of valuable data pertaining to the effect of cold-work on the conductivity of copper and some important copper alloys. In addition to being of engineering interest, the data are also important in supplying fundamental information that should be useful in relationship to the theory of metallic conduction. In this connection the large effect of cold-work in decreasing the conductivity of certain copper alloys, in particular those of zinc and aluminum, in comparison with the effect on copper, is notable.

It is well established that in metallic conductors electrical resistivity basically results from a scattering of the conduction electrons and that this scattering increases with the degree of departure from periodicity in the metallic lattice. One could explain the greater effect of cold-work in solid solution alloys as resulting from a greater disturbance in the perfection of the lattice periodicity occasioned by cold-work for the alloys than for the pure metal. Such an explanation does not carry far, for the reason that the greater departure from perfection in the alloys is still obscure. Other factors that may affect the resistivity change by cold-work are: structural changes accompanying deformation (grain fragmentation) and distribution changes in the two kinds of

* Bell Telephone Laboratories.

atoms, grossly, or over volumes very much smaller than the metallographic grain. In this connection Mott has pointed out that a random distribution of atoms may not be the one having the highest resistance. If small nuclei are present of about the magnitude of an electron wave (10 Å.) scattering may be more effective than for larger or smaller nuclei.

It is stated in the paper that in the copper-zinc alloys, which were the ones most extensively studied, the effect of working on conductivity is at least qualitatively related to the effect of working on tensile strength. Can it be assumed that the same internal process—that is, the mechanism of plastic deformation—is responsible for the change in each of these properties? If so, an understanding of the cause for conductivity changes might go far toward illuminating the obscurity existing in the dependence of strength properties on plastic deformation. The authors are to be congratulated upon having provided data that may stimulate consideration of the plastic deformation process from a viewpoint—electrical-conductivity changes—that perhaps has not received the emphasis it merits.

S. E. MADDIGAN,* Waterbury, Conn.—On page 236 the authors have suggested that incipient nucleation caused the small but definite hardening effect at temperatures below the visible recrystallization range. Such a concept was previously suggested by the writer⁹ to explain a small anomalous drop in conductivity previous to visible recrystallization in a long-time annealing study. In this work the anomalous conductivity effect appeared greatest in the lower ranges of reduction, whereas the hardening effect was much greater in the high reductions. This at first seems to be paradoxical if both effects are explained as due to incipient nucleation. Actually, however, there is no discrepancy.

Because of the much higher nucleation rate (as evidenced by the subsequent smaller annealed grain size), any effect due to incipient nucleation should increase with increasing degree of reduction. This is found to be true for the hardening effect. However, during the formation of incipient nuclei a recovery process is occurring in the matrix. This apparently has

little effect on the tensile strength, but is known to cause large increases in conductivity. Probably for high reductions this large recovery change masks out the much smaller change postulated as due to incipient nucleation. The nucleation effect might, however, be visible even for large reductions if observations were made at sufficiently frequent time intervals. Incidentally, the incipient nuclei as discussed later might be ordering nuclei rather than recrystallization nuclei.¹⁰

The authors have suggested that the mass of their results on copper-zinc alloys indicate an ordering effect at Cu₃Zn. They have wisely not attempted to offer this work as conclusive proof of such ordering. Certain points in the paper require further consideration in their relation to the ordering effect.

In Fig. 4c a minimum in the percentage of tensile strength change is found at the Cu₃Zn composition. This agrees with the suggested ordering, as ordering is sometimes accompanied by a hardening effect (p. 56 of ref. 1). Such an ordering might also be responsible for the hardening effect in the recovery range (Fig. 7).

In the previous work of the writer,⁹ a double-stepped change in conductivity was found during annealing as shown in Fig. 15. If two separate processes of nucleation and growth are assumed, a similar curve results, as shown in the figure. In the calculations the equation $F = A(1 - e^{-Kt})$ suggested by Johnson and Mehl¹¹ for processes of nucleation and growth has been used, with the values $A = 0.07$ and 0.15 ; $K = 20$ and 0.02 . It is known that conductivity is a function of ordering¹⁰ and if it is assumed that conductivity is also a function of the recrystallization process such a curve is readily explained. Since the ordering process requires an exchange of atom positions while the recrystallization process requires only reorientation and some slight motion of atoms, the first stage should be recrystallization, the second stage ordering. This would agree with the frequent observation that complete recovery of conductivity occurs in many cases at relatively low annealing temperatures.

Since both recrystallization and ordering are linked with diffusion, it is difficult to understand why such great differences should exist

* Research Physicist, Chase Brass and Copper Co.
⁹ S. E. Maddigan and A. I. Blank: *Trans. A.I.M.E.* (1940) **137**, 170.

¹⁰ J. Bardeen: *Jnl. Applied Physics* (1940) **11**, 88.

¹¹ W. A. Johnson and R. F. Mehl: *Trans. A.I.M.E.* (1939) **135**, 416.

in the K values used here. It might be suggested that recrystallization is associated not with diffusion but with the vibrational energy of the lattice. In this case the recrystallization

paper. After the so-called recovery stage, a straight-line relation also exists. Changes in conductivity with ordering are usually non-linear in relation to percentage reduction.¹

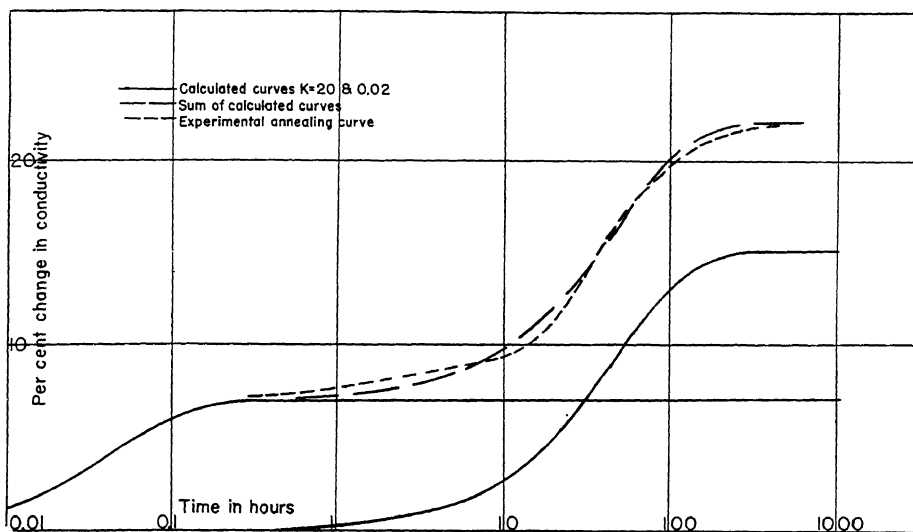


FIG. 15.—EXPERIMENTAL ANNEALING CURVE COMPARED TO CALCULATED NUCLEATION CURVE.

temperatures for various metals¹² would be related to the Debye characteristic temperatures.¹³ However, a comparison shows no relationship between the magnitudes of these two temperatures, whereas for the few cases given in the literature the energy of activation of diffusion increases in the same order as the recrystallization temperature.

It is also difficult to believe that the second stage of the conductivity change is not associated with recrystallization when the first visible new grains appear just at the beginning of this second steep rise in conductivity. On the other hand, it can hardly be considered that the first stage shown can be due to ordering. It should further be mentioned that the conductivity change in each stage is greater than the 2 to 3 per cent usually observed in other metals and alloys.

Fig. 2 shows a straight-line relation between percentage of reduction and conductivity change. The writer's work gave the results shown in Fig. 16. After complete annealing, a straight-line relation exists as in the present

This makes it doubtful whether either stage of the conductivity change can be associated with ordering.

In Fig. 6, for the 100°C. anneal the 75 per cent Cu-25 per cent Zn alloy shows less conductivity change than any of the others. Assuming ordering, this can be explained only by the formation of ordering nuclei even at this low temperature.¹⁰ At such a temperature the diffusion coefficient is extremely low¹⁴ and it seems doubtful that an observable interchange of atom types could occur in short-time anneals. It would therefore seem that an explanation of this point would require some process other than ordering.

The authors have mentioned the results of T. C. Wilson for 70-30 brass under high pressures. It is not clear how an ordering effect could appear at high pressures if it already exists at normal pressures with a critical temperature apparently above 900°C. This suggests that the annealing phenomena observed at normal pressures are not due to ordering.

In Fig. 11 an extremely large conductivity change is observed for the copper-cobalt alloy.

¹² R. S. Archer: *Metals Handbook* (1939) 200. Amer. Soc. Metals.

¹³ F. Seitz: *Modern Theory of Solids*. New York. McGraw-Hill Book Co.

¹⁴ F. N. Rhines and R. F. Mehl: *Trans. A.I.M.E.* (1938) 128, 185.

As pointed out by the authors, this can hardly be related to ordering. It may possibly be associated with a precipitation induced by working. One of the chief reasons for suggesting

H. L. BURCHOFF (author's reply).—Mr. Ellis' suggestion that the mechanism of plastic deformation may be responsible for the change in both strength and conductivity of materials is

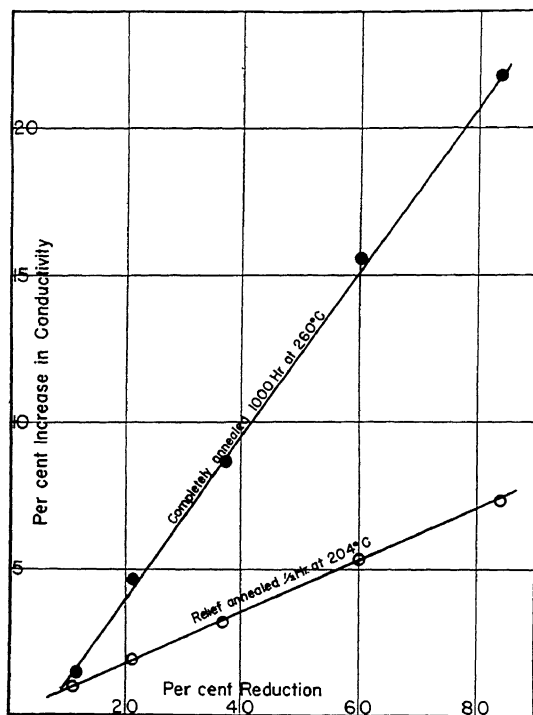


FIG. 16.—EFFECT OF DEGREE OF REDUCTION ON THE CONDUCTIVITY CHANGE FOR RELIEF ANNEALING AND COMPLETE ANNEALING.

ordering in the copper-zinc alloy is the large conductivity change effected by cold-work. In contradiction to this, we now have a still greater conductivity change in an alloy of which the explanation almost certainly lies elsewhere. In addition, the high conductivity changes in tungsten and molybdenum are well known. These are pure metals and hence do not involve ordering.

Of the various points discussed here, some seem to support the postulate of an ordered structure of the composition Cu_3Zn , while other points seem to support the opposite conclusion. A neutron transmission study such as that of Nix and Dunning¹³ would be of great value in reaching a conclusion on this subject.

interesting. It leaves a large field open for experimentation. Of course, as everyone knows, the actual mechanism of plastic deformation forms an elusive subject and is still being studied by numerous investigators.

Our work was of necessity, covering so many alloys, rather general in nature with regard to many of the materials. I do believe that a more careful study of the strain-hardening characteristics of all of them would be fruitful.

Dr. Maddigan has discussed various phases of the paper. If an alloy with ordered structure is deformed by cold-working, the ordering is reduced or possibly destroyed, owing to a relative displacement of atoms, which need not be great. The reordering during annealing would not require great atom movement and could coincide with recovery and recrystallization effects.

¹³ Nix, Beyer and Dunning: *Phys. Rev.* (1940) 58, 1031.

The lack of change in conductivity of the 75-25 Cu-Zn alloy when annealed at 100°C. is suggested to be due to formation of ordering nuclei. The small effects observed in material annealed at this low temperature, if real and capable of being differentiated, would seem to call for no active process in this alloy.

The large conductivity change reported for the quenched and drawn copper-cobalt alloy represents data for an isolated case and is worthy of further work to see if the results can be duplicated. The explanation of the large change does not lie in any brittleness of the alloy, as probably it does for the relatively brittle metal tungsten.

Low-temperature Oxidation of Single Crystals of Copper

By BENJAMIN LUSTMAN,* JUNIOR MEMBER, AND ROBERT F. MEHL,† MEMBER A.I.M.E.

(New York Meeting, February 1941)

THE study of the high-temperature oxidation of pure metals, intensively pursued experimentally since the pioneer work of Pilling and Bedworth¹ and supplemented by the recent theoretical work of Wagner² is now well advanced. The important field of low-temperature oxidation—i.e., oxidation extending only through the temper color range of thicknesses with the formation of thin oxide layers in the range from 0 to 1000–2000 Ångströms—has not, however, reached so satisfactory a state, owing largely to the experimental difficulties that attend the formation and study of thin films; most of the work has been performed on abraded specimens whose surface irregularities approximated the thickness of the films formed. It has been pointed out that the rates of oxidation of different crystal faces are different and that the difference may be related to the orientation relationships that obtain between the metal crystal and the superimposed oxide crystal; it has also been suggested that this orientation dependence should manifest itself in rates of oxidation and perhaps also of corrosion in aggregates bearing preferred orientations.^{3,4} An attempt to measure the rates of oxidation of different crystal faces of alpha iron demonstrated this difference in rate,⁴ but the dependence of rate on orientation was not simple; the method of

measuring thickness, consisting of a color comparison with barium stearate multi-films of known thickness, was not wholly satisfactory.

For these reasons it was felt that a study of the rate of oxidation of single crystals prepared with surfaces as smooth as possible, using a sensitive method giving true film thickness, should be profitable. Copper was chosen because of the ease of reduction of the primary oxide film and because the orientation relationships between metal and oxide and the composition of the oxide films formed at low temperatures are known; for thin films formed at low temperatures, Cu_2O alone occurs.^{22–24}

EXPERIMENTAL PROCEDURE

Various methods of surface preparation were attempted in order to obtain a surface that would oxidize uniformly and reproducibly. Electrolytic polishing by the method of Jacquet⁵ and electrolytic and mechanical polishing followed by annealing in vacuum and in purified hydrogen at various temperatures were tested. The procedure finally adopted consisted in a fine metallographic polish followed by an anneal in purified hydrogen at temperatures of 900° to 1000°C. for 12 hr. or more. The surface so produced was very bright and smooth, with no trace of specular etching (though some grain-boundary etching was observed); indeed, fine scratches produced by the final polish were entirely removed by the high-temperature anneal. After this treatment, the specimens were cooled in hydrogen to room temperature and placed in the oxidation furnace, where

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¹ References are at the end of the paper.

the air-formed film (never more than 10 to 20 Å. thick, as measured by the method described below) was removed by hydrogen reduction at 350°C. The specimen was

Laue back-reflection method after cutting, polishing, and annealing; these are shown in Fig. 2 plotted in a unit stereographic triangle.

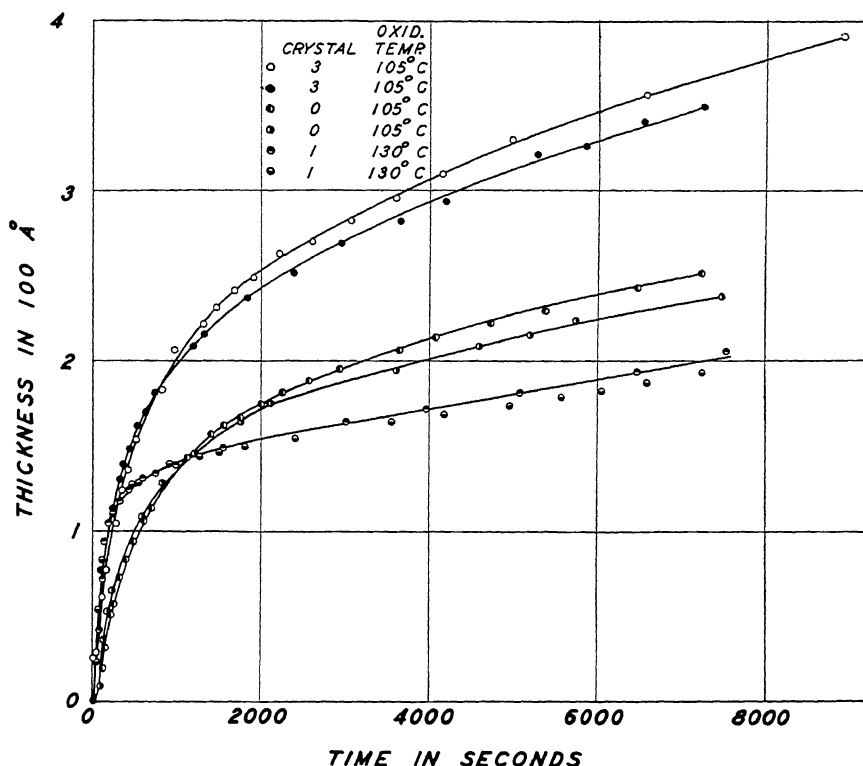


FIG. 1.—REPRODUCIBILITY OF OXIDATION CURVES.

then cooled to the oxidation temperature and dried air was admitted at a vigorous rate of flow. The air and hydrogen purification trains are shown in Fig. 3.

The reproducibility of oxidation curves obtained from surfaces prepared in this manner is shown in Fig. 1. The curves for crystal 3 and crystal 0 were obtained from the same specimens after repolishing and reannealing. The oxidation curves for specimen 1 were obtained from two different crystals of the same orientation.

Oxygen-free high-conductivity copper was used and single crystals were prepared by the Bridgman method. The orientations of their surfaces were determined by the

The apparatus used, including the purification train for the hydrogen and air, is shown schematically in Fig. 3. The specimens, of cylindrical shape, fitted snugly into a hole drilled into a block of copper around which the furnace windings were placed; the purpose of this arrangement was to provide the specimen with a source of heat in order to prevent a drift in the temperature of the specimen as the change from a hydrogen to an air atmosphere was made. The temperature of the crystals during oxidation was controlled within limits of $\pm \frac{1}{2}^{\circ}\text{C}$.

The incident light source was plane-polarized and reflected from the con-

tinuously oxidizing metal surface. On reflection from a metal surface, plane-polarized light is generally transformed to elliptically polarized light, the amount of

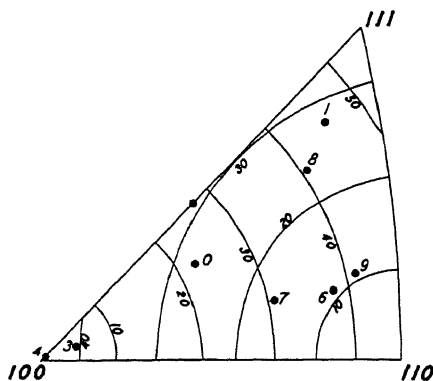


FIG. 2.—ORIENTATION OF COPPER CRYSTALS.

whose ellipticity depends on the refractive index of the metal and on the angle of incidence. The effect of a transparent film on the metal is to change the amount and nature of the ellipticity, which in the present case was measured by means of a quarter-wave plate and analyzing Nicol prism, with the addition of a half-shade system to increase the sensitivity of settings. By comparison of theoretical and actual ellipticity changes, both the refractive index and the thickness of the film could be obtained. Relations between the change in ellipticity and the film thickness and index of refraction were derived in a previous publication, by Leberknight and Lustman.⁶ The absolute accuracy of film thickness determination is controlled principally (indeed, almost exclusively) by the precision of measurement of the film index of refraction; knowledge of the latter to 10 or 20 per cent permits a determination of film thickness with an accuracy of 1 to 5 per cent.*

* Tronstad¹⁰ applied a similar experimental method to the study of films on metals; his interpretation of the polarimetric data, however, is valid only for very thin films, less than 50 Å. thick.

This method possesses several advantages over procedures previously employed to determine rates of film formation on metals. In the first place, its sensitivity of measurement is considerably greater than that of the other methods: thickness changes of one Ångstrom unit may be detected. The method used by Hinshelwood⁷ and others,^{8,9} involving measurement of change in pressure as the metal oxidizes at constant volume, is capable of comparable sensitivity at low pressures. However, this sensitivity is lost at high pressures and is hardly capable of accurate measurement at pressures above 0.1 atmospheres; furthermore, changes occurring within the film with changing pressure render the use of such a method questionable. The present method possesses the further advantage of allowing continuous, nondestructive measurement of film thickness during oxidation; this is of particular and obvious utility in determining the kinetic laws of film-forming processes. Of the methods commonly used, only that involving measurement of pressure changes and the temper-color method (consisting essentially of a comparison of the interference colors formed by the film with some standard) possess this same advantage. The applicability and disadvantages of the latter have been thoroughly reviewed by Evans;¹⁰ its insensitiveness, inaccuracy, and inapplicability to films below 300 to 400 Å. in thickness are serious drawbacks. In accuracy, the present method is approached only by the electrometric method of Miley¹¹ and Campbell and Thomas;¹² the latter method is capable of considerable accuracy and sensitivity but is destructive, discontinuous, and rather time-consuming. Thickness readings may be taken quickly (5 to 10 sec.), thus allowing close measurement of fast processes. Finally, small metal specimens of almost any shape may be used and their surface preparation can be closely controlled; the gravimetric method as used by Vernon,¹³ in which the weight of the film

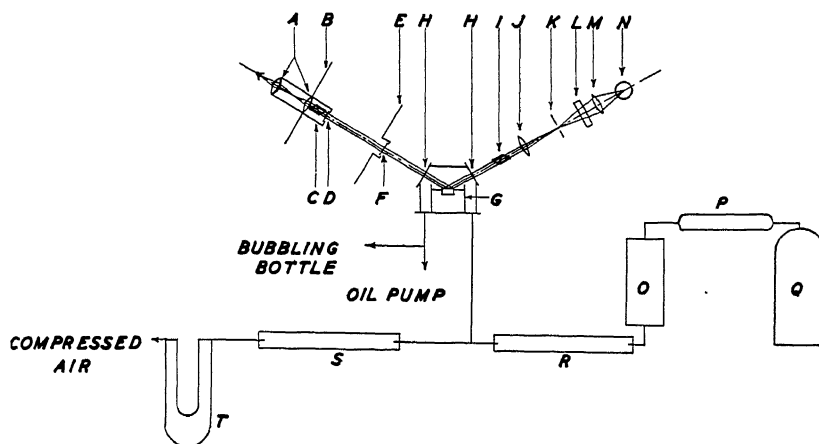


FIG. 3.—APPARATUS, INCLUDING PURIFICATION TRAIN.

- | | | |
|------------------------------|------------------------|-----------------------|
| A, telescope. | H, glass windows. | O, activated alumina. |
| B, analyzer scale. | I, polarizing Nicol. | P, platinum catalyst. |
| C, analyzing Nicol. | J, collimating lens. | Q, tank hydrogen. |
| D, half-shade. | K, slit. | R, barium oxide. |
| E, quarter-wave plate scale. | L, filter. | S, calcium chloride. |
| F, quarter-wave plate. | M, lens. | T, flow meter. |
| G, copper block furnace. | N, mercury vapor lamp. | |

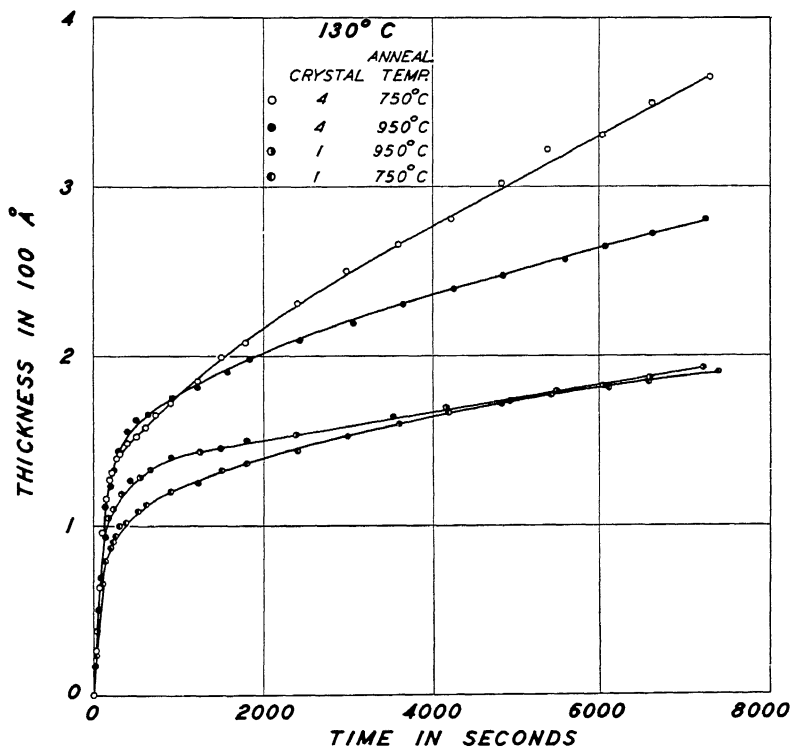


FIG. 4.—EFFECT OF ANNEALING TEMPERATURE ON OXIDATION OF COPPER.

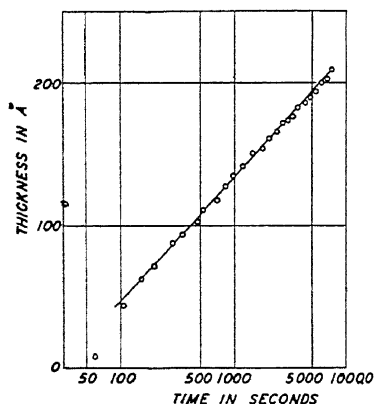
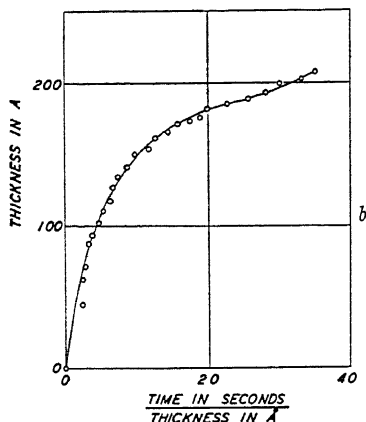
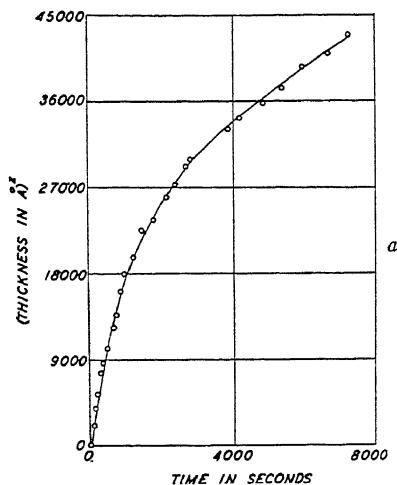


FIG. 5.—EFFECT OF DIFFERENT METHODS OF PLOTTING ON SHAPE OF OXIDATION CURVE OF CRYSTAL 14 AT 105°C .

formed is determined, requires the use of comparatively large specimens with large surfaces (such as sheet), the preparation of which would seem to be difficult. The disadvantages of the method used are: (1) It gives no information concerning the composition of the films; (2) it is applicable only to plane reflecting surfaces and cannot be used to determine film thickness on dull abraded surfaces; (3) it loses both sensitivity and accuracy with films of irregular thickness; (4) the determination of thickness from the observed optical properties requires rather cumbersome and involved calculations.

EXPERIMENTAL RESULTS

Effect of Annealing Temperature

Annealing the mechanically polished surface at temperatures above 950°C . yields a very bright, smooth surface; annealing at a lower temperature (750°C .) produces a surface showing slight specular etching.

Oxidation curves at 130°C . were made on specimens showing both types of surfaces (Fig. 4). The initial rate of oxidation is appreciably greater for the surface annealed at 950°C . than for the other surface, but later the rate is smaller. This difference, as is evident from comparison of Figs. 4 and 1, is greater than would be expected from the reproducibility of the oxidation curves. Thus, considering the sensitivity of the initial rate to slight differences in surface, it is to be surmised that measurements on the severely disrupted and stressed surface produced by abrasion should be of uncertain significance.

Form of the Oxidation Curve

Three principal types of equations have been proposed to explain the course of oxidation at low temperatures of metals forming protective films—the parabolic law,^{14,1}

$$l^2 = kt \quad [1]$$

the parabolic law corrected for the velocity of interface reactions,¹⁵⁻¹⁷

$$k_1 l + l^2 = k_2 t \quad [2]$$

and Tammann's logarithmic equation,¹⁸

$$t = a(e^{bt} - 1) \quad [3]$$

in which l is thickness, t time, and a , b and k are constants.

To decide which if any of these laws is obeyed, the oxidation curve of crystal 4 at 105°C. was plotted in the three following ways: square of thickness versus time, thickness versus time divided by thickness, and thickness versus the logarithm of time. The result is shown in Fig. 5; it is evident that equations 1 and 2 are not followed at any section of the curve, while, except for a brief initial period of less than 100 sec., the Tammann logarithmic law applies throughout.

In Figs. 6 to 10 are plotted the film thickness formed on all crystals at the oxidation temperatures 80, 105, 118, 130 and 155°C. versus the logarithm of time for one atmosphere air pressure. While the simple logarithmic law is obeyed initially in all cases to times of 1000 to 5000 sec., deviations generally occur at longer times. Except for crystal 9 oxidized at 105°C. (Fig. 7) the second part of the curve possesses a greater slope than the initial part. The complete course of the curves may in most cases be described by an equation of the form

$$\frac{1}{t} = \frac{1}{a_1 e^{b_1 t}} + \frac{1}{a_2 e^{b_2 t}} \quad [4]$$

It should be emphasized that it is the second part of such curves that is observed by a temper-color method of assessing thickness and that first led Tammann to the formulation of the simple logarithmic law.

The quantity to be chosen as expressing the rate constant for reaction curves obeying equation 4 deserves consideration.

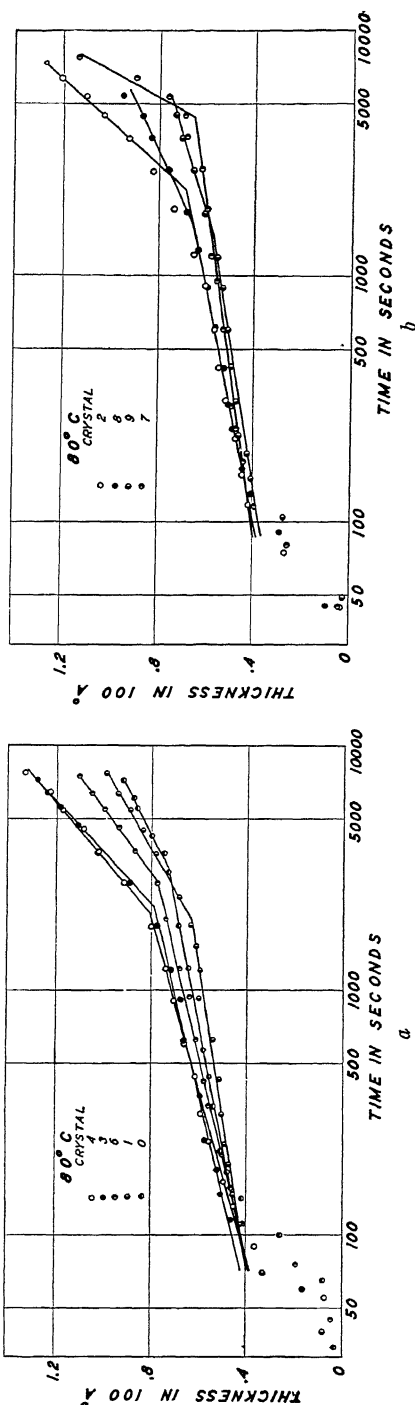


FIG. 6.—OXIDATION OF COPPER AT 80°C. ON LOGARITHMIC TIME SCALE.

Obviously the thickness of film formed at any given time will depend on both quantities a_1 and b_1 (excluding for the moment consideration of the later stages of oxida-

tion $\frac{1}{b_1}$, the slope of the oxidation curve when plotted on a logarithm of time abscissa scale, is more reproducible and

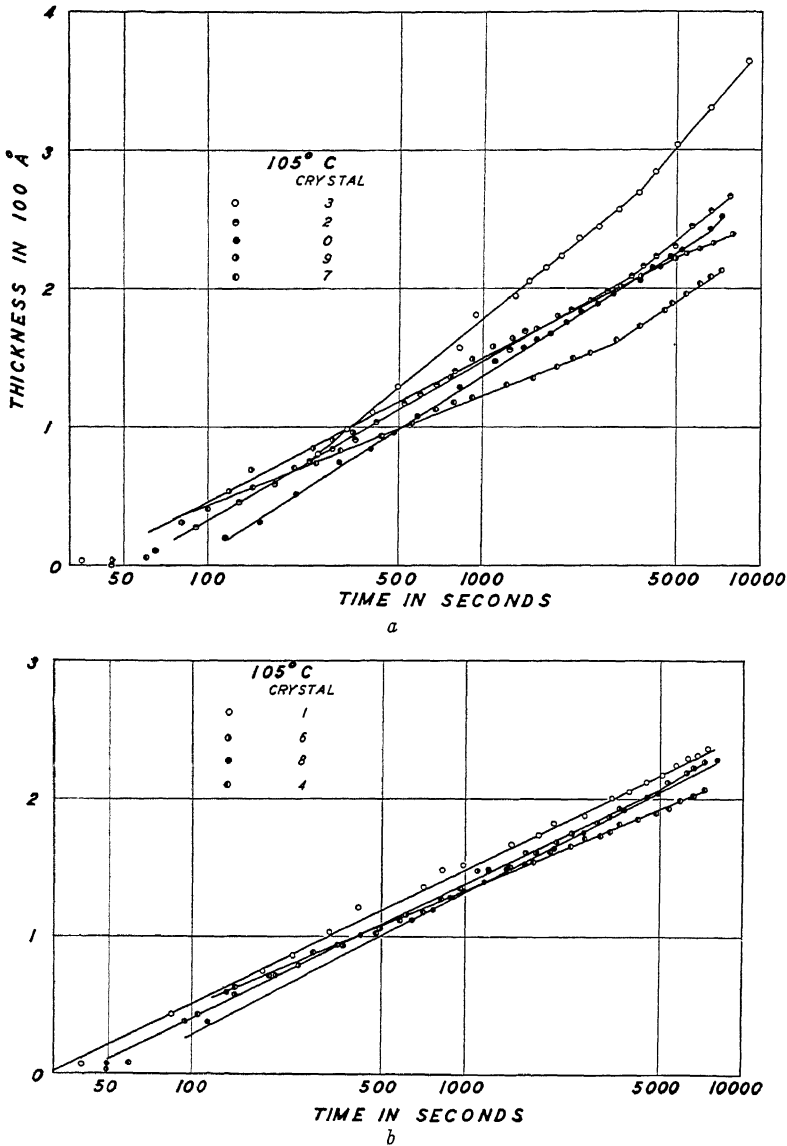


FIG. 7.—OXIDATION OF COPPER AT 105°C. ON LOGARITHMIC SCALE.

tion); thus neither of the quantities a_1 or b_1 alone will serve completely to specify the rate of oxidation. However, since the quan-

seems physically more expressive of oxidation rate than the quantity a_1 , which is the intercept of the curves on the abscissa at

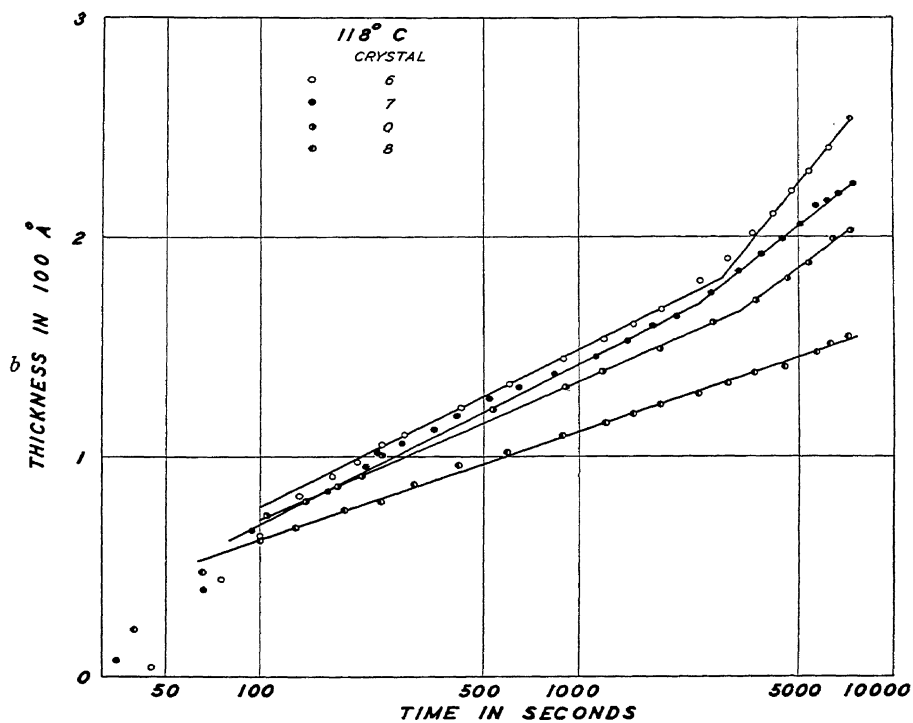
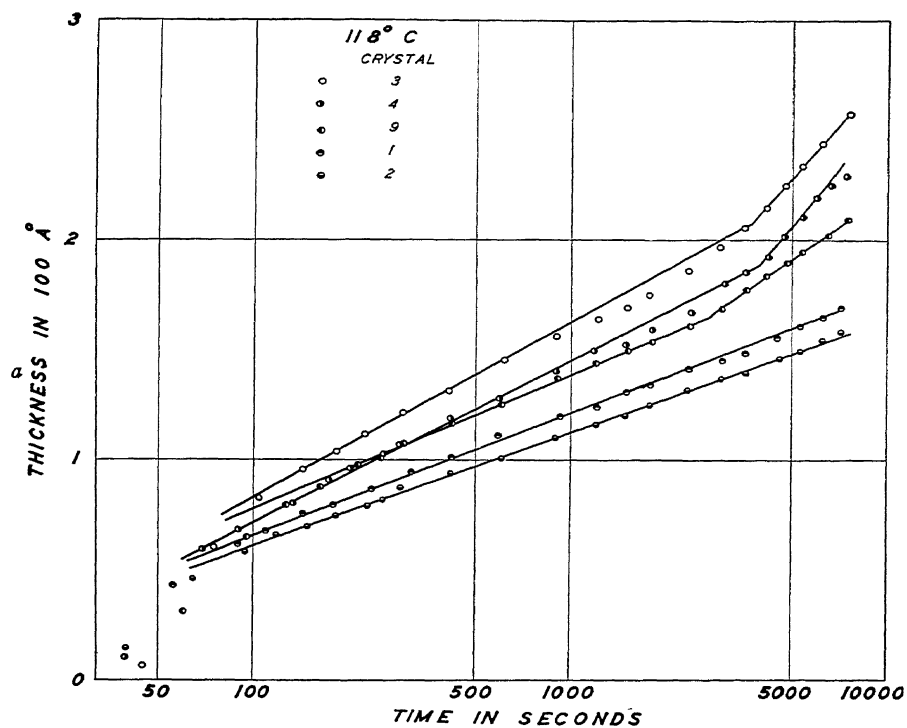


FIG. 8.—OXIDATION OF COPPER AT 118°C . ON LOGARITHMIC SCALE.

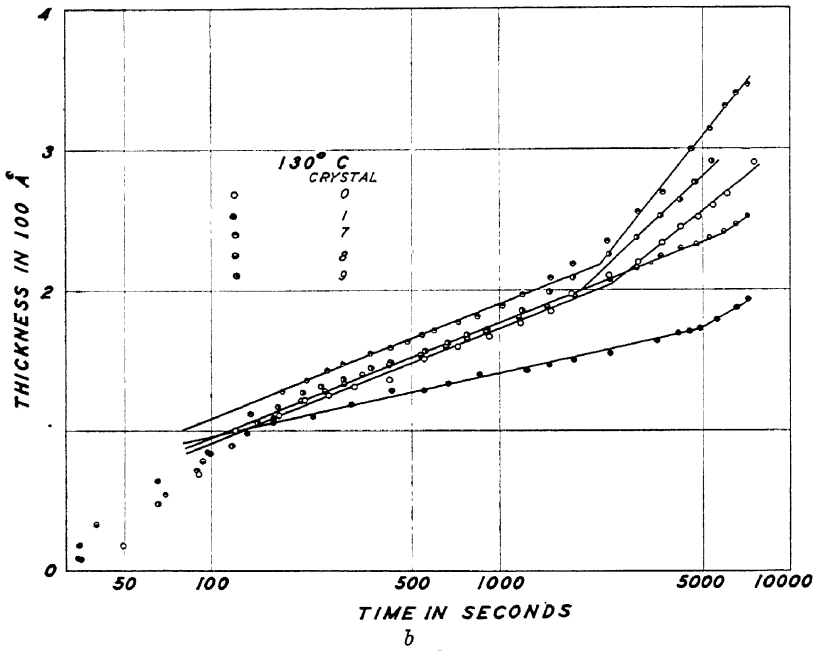
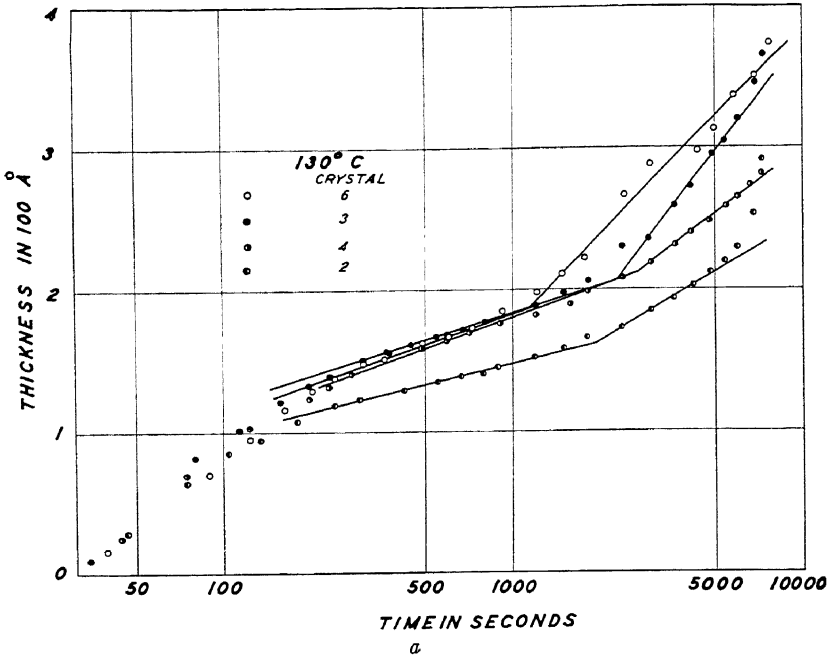


FIG. 9.—OXIDATION OF COPPER AT 130°C. ON LOGARITHMIC TIME SCALE.

zero thickness, the former was chosen as the rate constant. However, it should be emphasized that because of the partial dependence of rate on the quantity a_1

to the value of $\frac{1}{b_1}$, large values of a_1 accompanying large values of $\frac{1}{b_1}$; a_1 varies from about 1 sec. at 80°C. to 50 sec. at 155°C.

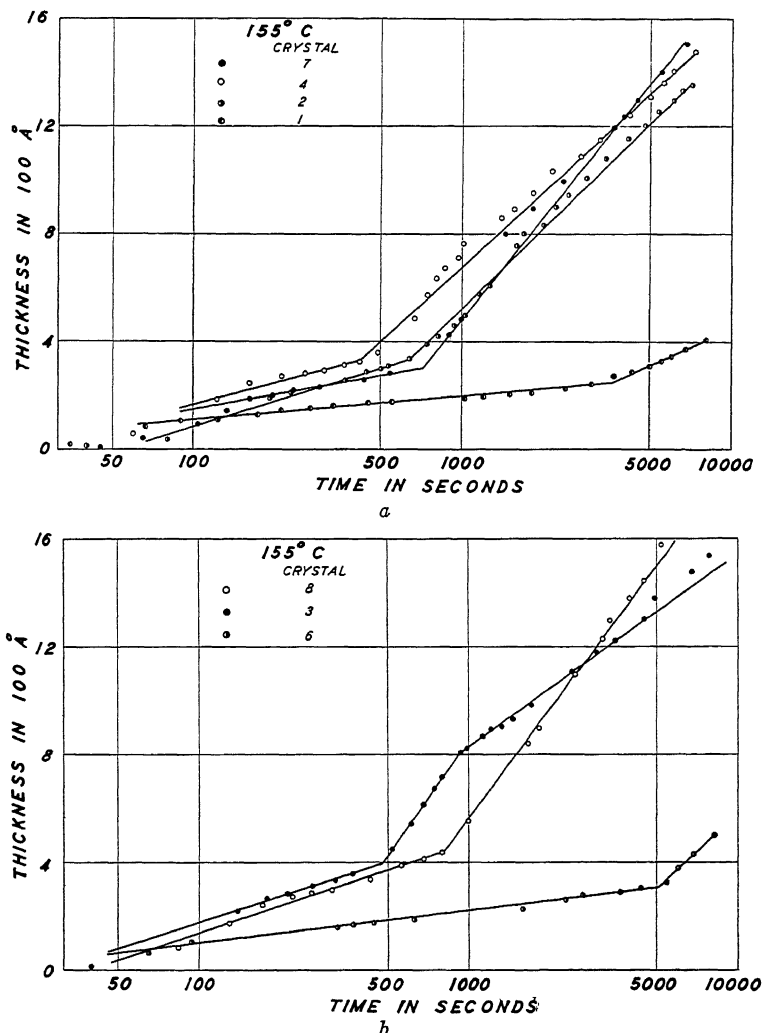


FIG. 10.—OXIDATION OF COPPER AT 155°C. ON LOGARITHMIC TIME SCALE.

at any given time, in spite of a greater value of the rate constant $\frac{1}{b_1}$, the oxide thickness attained by a given crystal may be less than that reached by a crystal showing a smaller value of the rate constant. In general, a_1 varies proportionally

Orientation Dependence of Oxidation Rate

The orientation relationships existing between Cu_2O and Cu after low-temperature oxidation have been thoroughly investigated. Mehl, McCandless and Rhines³ found that in scale formation on copper the

Cu_2O lattice was oriented in the same way as the underlying copper lattice. This is identical with one of the orientations observed later by Moore,²² who found on

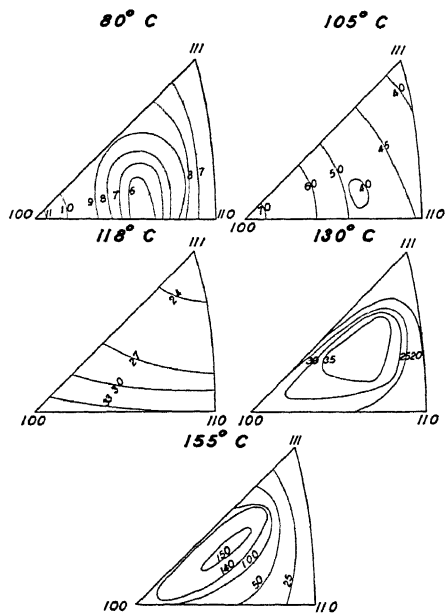


FIG. 11.—ORIENTATION DEPENDENCE OF OXIDATION RATE PLOTTED IN UNIT STEREOGRAPHIC TRIANGLE.

Fine lines are contour lines of equal slope of logarithmic oxidation curves $(1/b_1)$ and figures refer to magnitude of $1/b_1$ in Ångströms.

(100) planes of copper the orientation relationship $(111) \text{Cu}_2\text{O} \parallel (100) \text{Cu}$ and $[110] \text{Cu}_2\text{O} \parallel [100] \text{Cu}$, while he found on (110) and (111) planes of copper the orientation relationship $(100) \text{Cu}_2\text{O} \parallel (100) \text{Cu}$, and $[100] \text{Cu}_2\text{O} \parallel [100] \text{Cu}$. This confirmed the orientations reported somewhat earlier by Yamaguchi²³ and Thiessen and Schütza.²⁴ Thus, except for orientations around the (100) plane of copper, the orientations of the copper surfaces shown in Fig. 2 are those of the Cu_2O film formed on each surface.

The slopes of the initial parts of the curves in Figs. 6 to 10 inclusive, (corresponding to $\frac{1}{b_1}$ in equation 4) may be taken

as expressing the rate of oxidation, and these are plotted in the appropriate position in the unit triangle in Fig. 11 and contour lines of equal oxidation rate are drawn. The minimum in the rate at 80°C. apparent in the center of the stereographic triangle almost disappears at 105°C., at which temperature the oxidation rate seems to be inversely proportional to distance from the (100) pole. At 118°C. the (111) pole apparently is a singular axis, the oxidation rate increasing with angular separation from this direction; however, the same trend of the quantity $\frac{1}{b_1}$ is noted as at 105°C.—i.e., (100) planes of copper oxidize faster than (110) planes, with (111) planes showing minimum rate. At 130°C. the maximum in the oxidation rate shifts from the (100) pole to approximately the position occupied by crystal o (Fig. 2); the same dependence is shown at 155°C.

Temperature Dependence of Oxidation Rate

Dunn²⁵ applied the Arrhenius equation, which has been shown to be applicable to all diffusional processes,⁴³ to the explanation of the temperature variation of oxidation rate. This equation states that

$$W = Ae^{-Q/RT} \quad [5]$$

in which W is the oxidation velocity, A the action constant, e the base of natural logarithms, Q the heat of activation, R the gas constant, and T absolute temperature. Thus a plot of the logarithm of oxidation velocity versus the reciprocal of absolute temperature should give a straight line if the oxidation rate depends on a simple activated diffusion through the oxide film. Pilling and Bedworth¹ had previously expressed the temperature variation of scaling rate by an exponential equation of another form.

In Fig. 12 the logarithm of the oxidation rate constant $\left(\frac{1}{b_1}\right)$ has been plotted against the reciprocal of the absolute temperature

for each of the crystals studied; obviously, since a straight-line plot does not result, a growth process is occurring, which is not explicable by a classical temperature variation. It will be noted that a minimum in the oxidation rate occurs in the neighborhood of 105° to 155°C. for each crystal face. It should be emphasized here that this minimum is peculiar to the quantity $\frac{1}{b_1}$; for almost every crystal the oxide thicknesses formed after a given oxidation time increase quite normally with increase in reaction temperature, though again not according to the activation equation (Eq. 5). That Tammann and Köster¹⁸ found a discontinuity in the oxidation rate of copper at 205° to 220°C. and Dunn²⁶ at 209° to 241°C. , whereas in the present investigation the minimum was observed at 105° to 155°C. , may perhaps be ascribed to differences in the character of the initial metal surface resulting from different modes of preparation.

The oxidation-rate constants, $\frac{1}{b_2}$, for the latter parts of the curves of Figs. 6 to 10 are plotted in Fig. 13; this quantity likewise does not follow the Arrhenius equation. As a measure of the rate of chemical attack of copper by oxygen, the rate of thickening of the oxide within the first 3 min. of oxidation was chosen; again the activation equation (Eq. 5) was not followed, as is shown in Fig. 13.

Effect of Oxygen Pressure

The rate of oxidation of crystal 4 was determined at 118° and 105°C. at various air pressures up to one atmosphere. The pressures were obtained by pumping through suitable capillaries and constricted tubes, so that a vigorous rate of flow of air was maintained past the specimen. Fig. 14 shows the results obtained at three values of the partial pressure of oxygen; a maximum in the oxidation rate with decreasing pressure of oxygen may be observed. This is

better shown in Fig. 15 for the oxidation of crystal 4 at 105°C. and Fig. 16 at 118°C.

The existence of a maximum rate of oxidation at about 0.015 atmospheres of

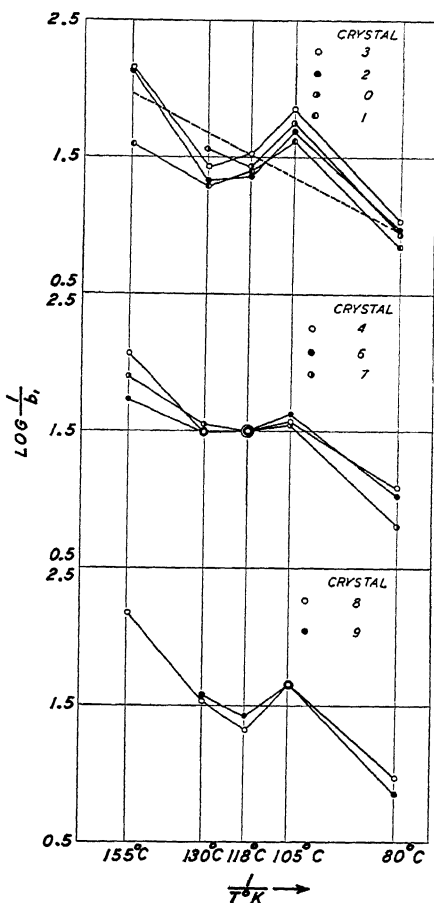


FIG. 12.—VARIATION OF OXIDATION RATE ($1/b_1$) WITH TEMPERATURE.

oxygen may be noted for both temperatures; for all pressures at these two temperatures the logarithmic law (Eq. 4) again is obeyed for the greater part of the curves. In Fig. 17 the oxidation-rate constant ($\frac{1}{b_1}$) has been plotted against partial pressure of oxygen. While at higher pressures crystal 4 oxidizes faster at 105°C. than at 118°C. , at the lower values of oxygen pressure the oxidation-rate con-

stant increases normally with increase in temperature; undoubtedly it was for this reason that Wilkins and Rideal⁸ (whose experiments were all conducted at low

by a parabolic time law and whose rate of thickening increases with temperature according to the Arrhenius equation (Eq. 5) must obviously grow by a mecha-

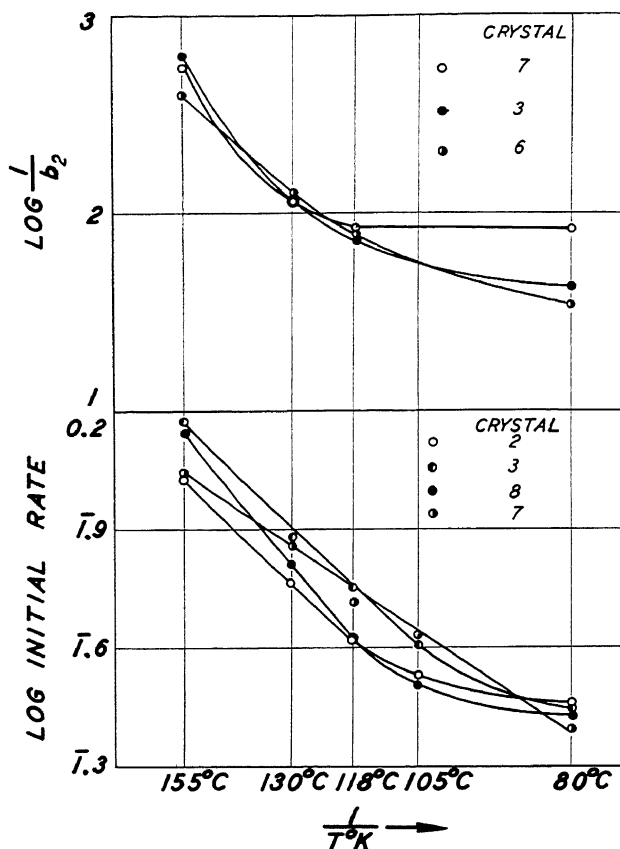


FIG. 13.—VARIATION OF FINAL OXIDATION RATE (I/b_2) AND INITIAL RATE WITH TEMPERATURE.

pressures) observed no minimum in the variation of oxidation velocity with temperature.

DISCUSSION OF RESULTS

From a consideration of the complexity of the experimental data, it is immediately obvious that no simple theory based upon ionic and electronic diffusion such as is so successfully applicable to the explanation of scaling velocities of metals will serve to explain the low-temperature oxidation of copper. Scales that increase in thickness

nism different from that of films that form according to an exponential time law and by a complex temperature dependence of growth. Therefore the following discussion will be restricted to a consideration of the similarities in the low-temperature oxidation behavior of metals and of the theories that have been proposed.

Since the presentation of the logarithmic law by Tammann and Köster in 1922, it has been continually attacked and questioned. Most of the objections were based on the method used by Tammann for its

experimental verification—the temper-color method—objections that for the most part are valid.¹⁰ However, it is not certain that the corrections that would have to be made to Tammann's experimental data would vitiate his conclusions as to the shape of the oxidation curve. It has been shown in the preceding paragraphs that copper oxidizes logarithmically in the temperature range 80° to 155°C. By the same experimental method a few oxidation curves also have been obtained for single crystals of iron at a temperature of 300°C. The shape of these curves when plotted on a logarithmic time scale is shown in Fig. 18; the validity of the exponential law in explaining the oxidation of iron may be recognized. Similarly, Vernon, Akeroyd, and Stroud²⁷ showed that below 200°C., a temperature that Vernon¹³ believed marked a change in the crystal structure of Fe_2O_3 , iron oxidizes logarithmically. Steinheil⁴¹ determined the course of oxidation of thin films of aluminum by the change in their transparency; his curves are shown replotted on a logarithmic time abscissa scale in Fig. 18. Vernon, Akeroyd, and Stroud²⁷ established gravimetrically the applicability of the logarithmic law to the oxidation of zinc at 125° to 225°C. Thus Eqs. 3 and 4 have been found to be generally valid for the explanation of the low-temperature oxidation of copper, iron, aluminum and zinc by three very different experimental techniques; it would therefore seem correct to state tentatively that *all metals forming protective oxides oxidize according to the logarithmic law at low temperatures*. This is the first generalization in the oxidation behavior of metals that requires explanation.

Several explanations have been proposed to account for the logarithmic law. Wagner³⁰ considered that Tammann's law may be a matter of purely accidental reality and that it may arise from instability of the primary oxide layer due to the following causes: (1) recrystallization or sintering phenomena in the film; (2) transition from

unstable to stable crystal modifications; (3) formation of a higher oxide at larger film

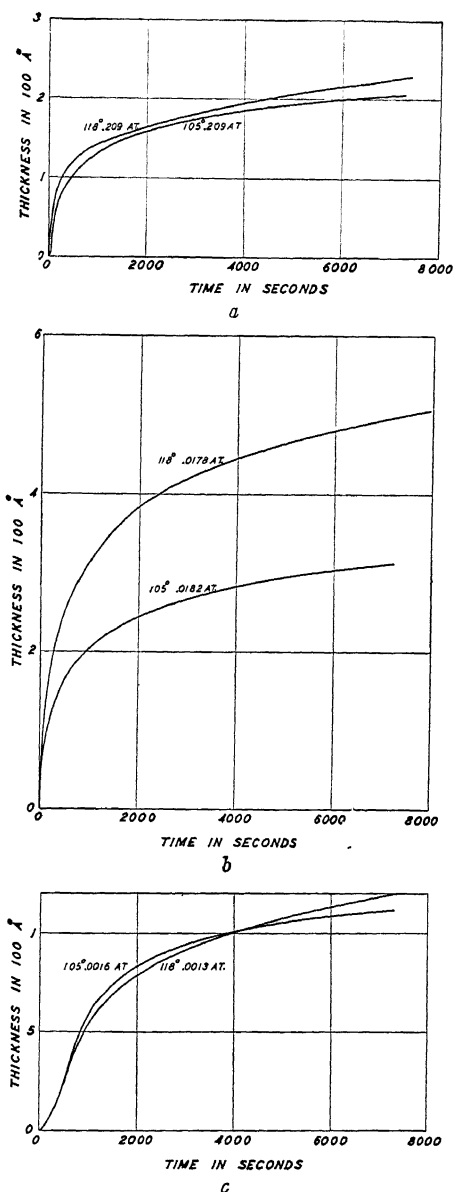


FIG. 14.—OXIDATION OF COPPER AT PRESSURES AND TEMPERATURES INDICATED.

thicknesses. The first possibility may be ruled out immediately; however valid the assumption of sintering might be for films

formed on strained, abraded, polycrystalline surfaces, in the present work, where strain-free, single-crystalline surfaces were used, a single-crystalline oxide must result.

crystal 4 several orientations would result from such a process, since the orientation relationship obtaining on (100) planes leads to several different possibilities of match-

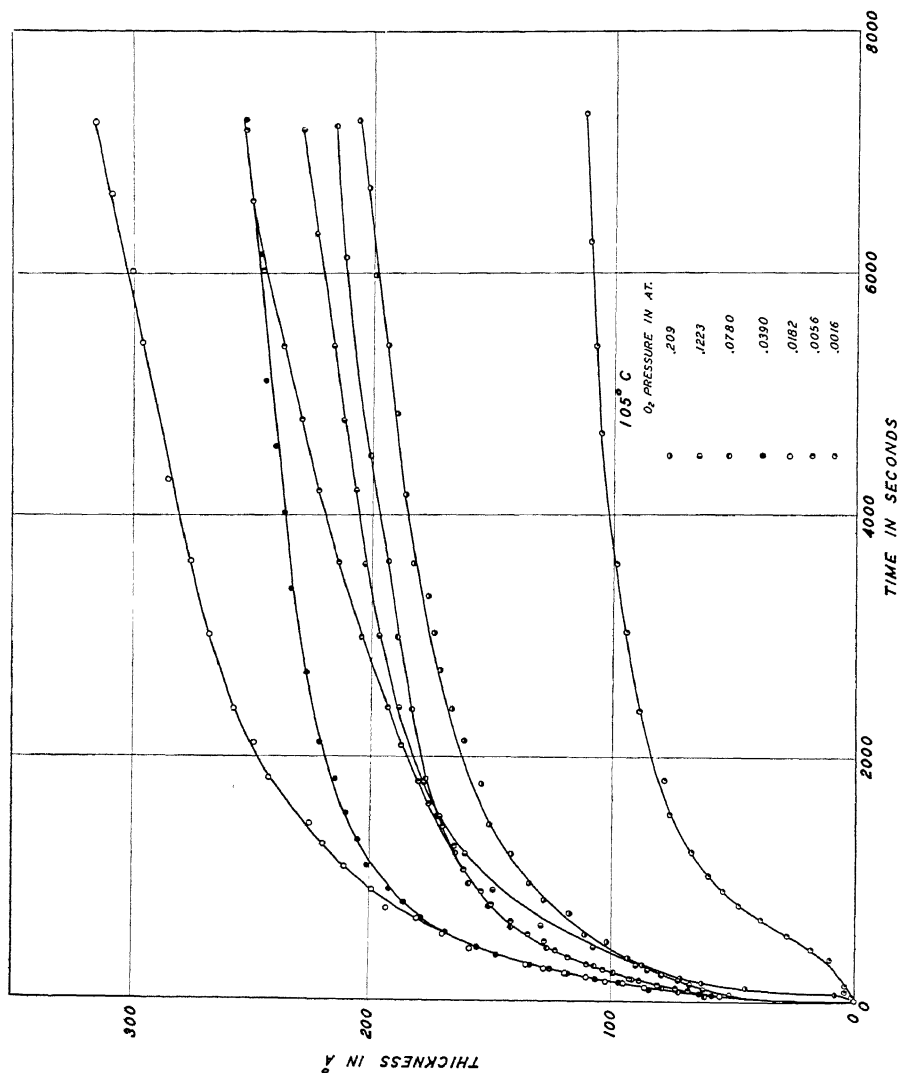


FIG. 15.—OXIDATION OF COPPER AT VARIOUS PRESSURES AT 105°C.

Even if it is supposed that growth of the films occurs from a number of points on the metal surface, for all orientations except that of crystal 4 a single crystal of oxide must result, since the orientation of the oxide is the same as that of the metal. For

ing; however, inasmuch as crystal 4 shows the same behavior on oxidation as all the other crystals, this fact would seem to be of little importance in determining the manner of oxidation. Furthermore, since it has been shown³ that single-crystalline

oxide films remain single crystalline even after they have grown into thick scales, recrystallization within the primary oxide film is obviously excluded. Possibilities 2

have shown that at Cu_2O thicknesses less than 400 Å. the oxide consists entirely of Cu_2O , while in the range 400 to 800 Å. traces of CuO may occur; only above

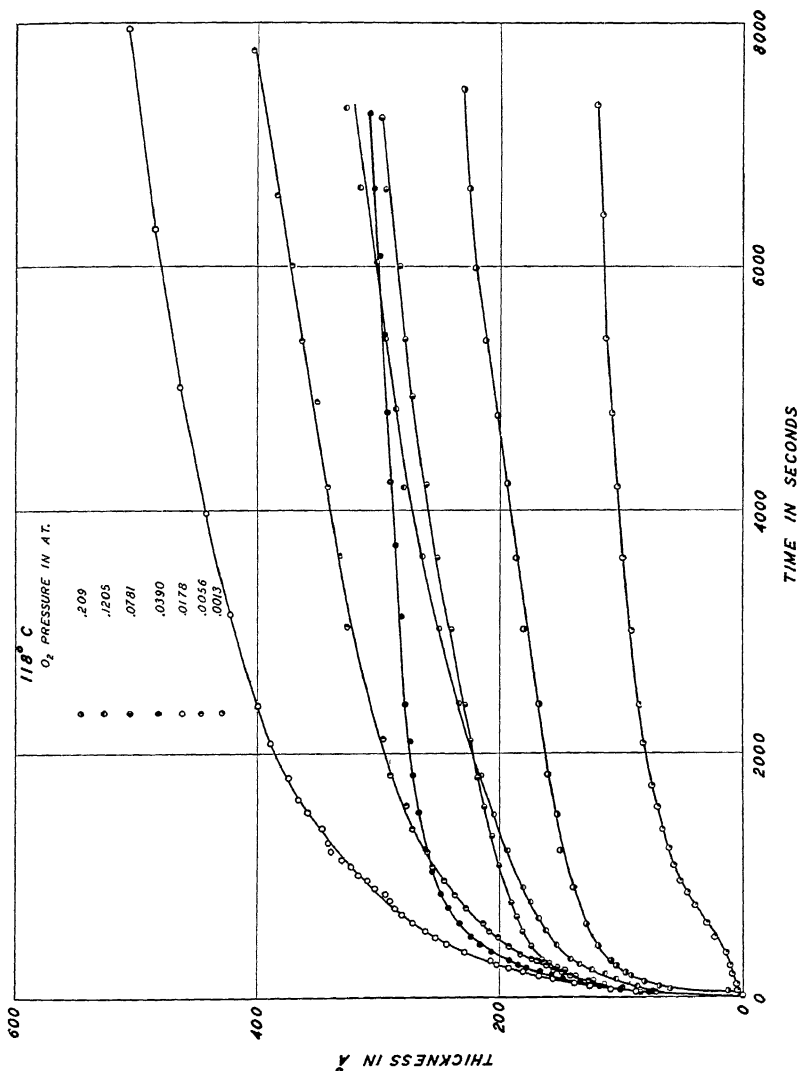


FIG. 16.—OXIDATION OF COPPER AT VARIOUS PRESSURES AT 118°C.

and 3 may likewise be ruled out on the basis of electron-diffraction studies, which indicate that the films formed at low temperatures on copper are composed of cubic Cu_2O predominantly at all oxidation times and temperatures. Cruzan and Miley⁴²

800 Å. thickness of film definite amounts of CuO always appear and then only in very small amounts. In the present experiments the oxide thickness attained 400 Å. only at 155°C.; during the initial logarithmic part of the oxidation curves, it may be safely

assumed therefore that the film consists merely of Cu_2O .

If it is assumed that the ionic concentration gradient within the film is an exponen-

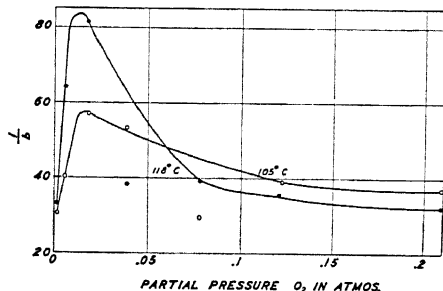


FIG. 17.—VARIATION OF OXIDATION RATE (I/b_1) OF COPPER WITH PRESSURE.

tial function of distance, and that the simple diffusion laws may be applied to such a concentration gradient, an equation of the form of the logarithmic law may be derived; it was thus that Tammann justified his equation and that Vernon and his coworkers²⁷ explained the oxidation behavior of zinc at low temperatures. However, it is doubtful whether either of these assumptions is valid.¹⁹ Certainly it has been shown definitely³¹ that if oxidation results from movement of ions through the oxide in conformity with Fick's laws, with diffusion velocity independent of the concentration of anions or cations, the parabolic law will result. There is, however, adequate evidence that the diffusion constant will not have a fixed value throughout the film. Rother and Bohnke³² have shown that electrical conductivity in thick oxide scales formed on copper varies markedly within the oxide as shown in Fig. 19. That a similar condition obtains in the thin films formed in the present investigation may be inferred from Fig. 20. The method of determining thickness permitted also a rough determination of the index of refraction of the film; it was found that the results could be satisfactorily expressed by constancy of the real part of the index n (with

a value of 2) and by a variation of the absorption index k as shown in Fig. 20. If it is assumed that variation of the light absorption within the film is due for the most part to a change in the number of free electrons, the apparent average absorption will tend to trace a course with increasing film thickness similar to the curve of electrical conductivity (which is also proportional to the number of free electrons or of missing electron sites) within the film. From the parallelism of conductivity and diffusion rate³³ one would thus expect a variation of the diffusion coefficient with concentration; if such a variation were introduced into the formal diffusion laws, a form of the resulting oxidation equation might well follow which would differ from the parabolic law. It must, however, be noted that in spite of the known variation of conductivity (diffusion rate) with concentration in thick films the scaling of copper generally follows a parabolic equation. An explanation of the logarithmic law by ionic diffusion processes occurring within the film is thus a possibility, but at present only an obscure one.

Mott³⁹ has recently proposed a theory that promises to be of importance in explaining the low-temperature oxidation of metals. His theory is founded primarily on the premise that in thin films the ionic and electronic concentration gradients through the film may be independent of each other, whereas in thick films, because of space charges that would be set up by unequal gradients, the ionic and electronic gradients are interdependent. Mott assumes that in thin films the rate of film growth is controlled by the rate at which electrons can leave the metal surface and ionize absorbed oxygen atoms at the oxide-gas interface. The probability that an electron that leaves a metal surface with an energy W (the work function) will penetrate by the tunneling effect a barrier of height U and thickness l (the film thickness) is proportional to the expression

$$e^{-\frac{4\pi l \sqrt{2m(U-W)}}{h}}$$

where m is the mass of the electron and h is Planck's constant. The derivation of the

change in slope at 200°C. in the plot of log of oxidation rate of iron versus the reciprocal of oxidation temperature, which again was attributed to a change in the crystal

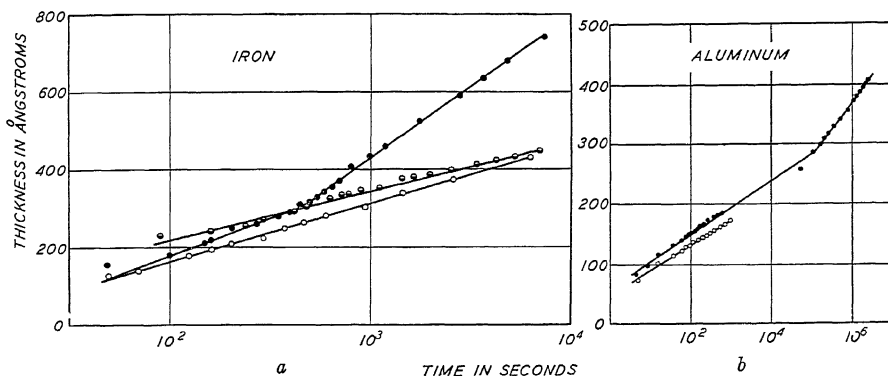


FIG. 18—OXIDATION OF IRON (LUSTMAN AND MEHL) AND ALUMINUM (STEINHEIL⁴⁶) ON LOGARITHMIC TIME SCALE.

logarithmic law from such an expression is obvious. It will particularly be noted that the factor corresponding to $1/b_1$ in Eq. 4 $\left(\frac{h}{4\pi \sqrt{2m(U-W)}}\right)$ depends only on the temperature-independent factors U and W —the energies required for an electron to penetrate the oxide and to leave the metal. Thus, by Mott's theory, no temperature dependence of $1/b_1$ is predicted.

The second generalization that may be proposed concerns the temperature dependence of oxidation rate at low temperatures. It was shown above that a minimum in the oxidation rate of copper exists at 105° to 155°C. Dunn²⁰ ascribed a similar effect to sintering or grain growth within the film; such an explanation is obviously inapplicable to the single-crystal oxide films formed here. Vernon, Akeroyd and Stroud²⁷ recently observed a similar minimum in the oxidation rate of etched abraded and anodically polished zinc surfaces at temperatures of 120° to 225°C. This effect the latter authors attributed to a change in the crystal structure of ZnO from amorphous below 225°C. to hexagonal above this temperature. Vernon¹⁸ also reported a

structure of Fe_2O_3 from the alpha form above 200°C. to the gamma form below this temperature. In the case of the oxide formed on copper, numerous exhaustive electron-diffraction and X-ray investigations disclosed no change in the crystal structure of the predominant oxide phase Cu_2O from the lowest to the highest temperatures of oxidation. From the fact that deviations from the expected oxidation behavior occur within so close a temperature range, 105° to 225°C., for metals as dissimilar as copper, zinc, and iron, forming dissimilar oxides, it would seem more inviting to attribute these common differences to some mechanism common to the oxidation of each of these three metals. Certainly no minima should occur if the oxidation rate is controlled by ionic diffusion through the film, in which case Eq. (5) should hold. Mott's theory, on the other hand, predicts that $1/b_1$ should have a constant value independent of temperature. It is obvious that no theory yet proposed is adequate to explain the temperature dependence of film formation on metals. Thus if the data on the three metals listed are considered illustrative of a general behavior,

it may be hypothesized that *the oxidation rate of metals at low temperatures changes discontinuously with temperature.*

It was found in the experiments on copper

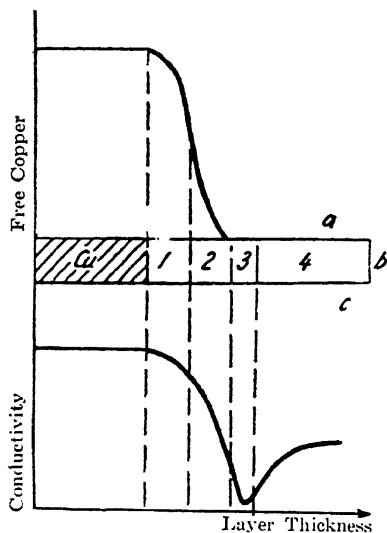


FIG. 19.—VARIATION OF FREE COPPER CONTENT AND CONDUCTIVITY IN Cu_2O FILM (RUTHER AND BOHNKE³⁷).

that in general the oxidation curves resolved themselves into two straight-line portions when plotted on a logarithmic time scale, the time law consisting of a sum of two exponential expressions. As is evident from Fig. 18, iron and aluminum both show the same type of behavior. Curves presented for the oxidation of zinc and of iron (below $200^\circ\text{C}.$) by Vernon, Akeroyd, and Stroud²⁷ indicate that similar curves would have been obtained if a more sensitive measuring method had been used. Thus the third characteristic of oxide film formation may be that *the course of oxidation of metals at low temperatures is given not by one but by at least two exponential expressions.* Again none of the theories, including Mott's, predicts this result.

It has been suggested that the two exponential sections may arise from the formation of CuO at longer oxidation times. If this were true, the oxidation velocity

should be smaller at greater thicknesses because of the low ionic mobility in CuO ; however, it has been found that the second logarithmic section is always of greater slope than the first. Further, Cruzan and Miley⁴² have shown that CuO is not present in oxide films of the thicknesses produced in the present investigation.

A fourth characteristic of the low temperature oxidation of metals may be that *smooth surfaces oxidize more slowly than rough surfaces.* Thus it was shown earlier in this paper that an etched copper surface oxidizes at a slower initial rate, but faster final rate than a smooth surface. A similar effect was noted by Vernon, Akeroyd, and Stroud²⁷ in the low-temperature oxidation of zinc. In the latter, the oxidation curves of anodically polished surfaces (measured over long time periods) were found to lie at lower thicknesses than those obtained from either abraded, or abraded and etched surfaces. From the slower final oxidation rate of smooth strain-free surfaces as compared with that of rough or etched strain-free surfaces, which apparently is valid for the low-temperature oxidation of both copper and zinc, one might offer the generalization that the effect of manner of surface preparation is predominantly one of surface geometry, smooth surfaces reacting more slowly than serrated surfaces. The well-known effect of low-temperature reduction of an oxide film on the subsequent acceleration of oxidation may be attributed thus to a microscopic surface roughening.

Finally, it may be stated as a fifth generalization that *oxidation rate varies with crystal orientation in a manner not to be predicted in a simple way from the crystallography of the oxides or from the oxide-metal orientation relationships.* The rate of oxidation of copper single crystals at 105° , 118° , 130° and $155^\circ\text{C}.$ was found to vary with angular separation from some singular axis, the $[100]$ direction at $105^\circ\text{C}.$, $[111]$ at $118^\circ\text{C}.$, and the pole of crystal o at 130° and $155^\circ\text{C}.$ Braun³⁹ found that the elec-

trical conductivity of rock salt in the [100], [110], and [111] directions was in the ratio 6:4:3, which is explicable by a mechanism in which conduction occurs in a cube direc-

conductivity, Dünwald and Wagner²⁸ connected with a state of disordering of the oxide involving empty places in the Cu^+ lattice and in the electron lattice (electron-

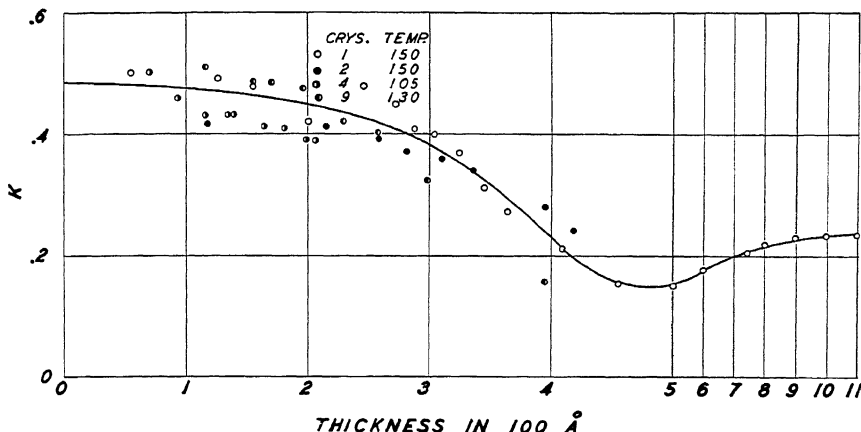


FIG. 20.—VARIATION OF ABSORPTION INDEX OF Cu_2O FILMS WITH THICKNESS.

tion only—i.e., by a mechanism in which the [100] direction is a singular direction, as in the oxidation experiments above. However, the reason for the change in the singular axis with oxidation temperature is obscure on the basis of this explanation; furthermore, Joffe³⁵ found that the conductivity of cubic crystals is isotropic. Gwathmey and Benton²⁸ found, by observing the temper colors on a copper single-crystal sphere oxidized at various pressures and temperatures, even more complicated orientation dependencies. Mehl and McCandless,⁴ studying the oxidation of iron, likewise found a complex orientation dependence, which again could not be reconciled with relative oxide-metal orientation.

Because of the paucity of experimental data on the variation of oxidation rate of metals with oxygen pressure, the generality of the effect of pressure noted for the oxidation of copper cannot be assumed. It has been observed that at high temperatures the scaling rate of copper increases with pressure as the seventh root of that quantity.²⁹ This, in the analogous case of

defect places). However, Schottky and Waibel³⁶ found that Cu_2O shows electron excess conduction below 500°C ., which, interpreted in terms of lattice disordering, could mean excess copper ions in the lattice above the stoichiometric composition (or a deficit in oxygen ions) and free electrons. This state of disordering is similar to that which exists in ZnO and CdO , the conductivity of which Baumbach and Wagner³⁷ found to increase with decreasing pressure. The increase in rate of oxidation with decreasing pressure at high pressures in the present investigation is thus explicable. It should be noted that this mechanism explains only the variation of oxidation rate at high pressures; the decrease observed at lower pressures must obviously depend on some other process. Whatever this other process might be, it cannot be one that would occasion a radical change in the manner of oxidation, for the oxidation curves were observed to be substantially logarithmic throughout the range of pressures investigated. It is possible, however, that with decreasing pressure the solid

solution composition range of Cu_2O becomes narrower; the decrease in the concentration gradient would tend to cause a decrease in oxidation rate.

MECHANISM OF INITIAL REACTION

The process by which oxygen molecules react with clean metallic surfaces to form the initial oxide film has recently been studied by Roberts.³⁸ On exposure of a clean metallic surface to oxygen, a discontinuous two-dimensional atomic film of oxygen forms, and by diffusion through this film the initial three-dimensional oxide results. On hydrogen-covered tungsten wire, this adsorption of oxygen was found to be a comparatively slow process. Confirmation of these conclusions was found in the present investigation. When air was admitted to the specimens after reduction but without a preliminary evacuation of the hydrogen, a period of 30 to 40 sec. was observed during which the specimen surface showed no apparent change—i.e., no refracting film 1 to 2 Å. thick was formed; after this initial period, oxidation began at a maximum rate. Presumably during this initial period the adsorbed hydrogen film was being replaced by an absorbed oxygen film. When the hydrogen was first evacuated the oxidation process began immediately at maximum rate; most or all of the adsorbed hydrogen film was apparently driven off.

At the very lowest pressure investigated, an entirely different mechanism of initial oxide formation is operative. From Figs. 20, 21 and 22, it may be seen that at 0.0016 to 0.0013 atmospheres partial pressure of oxygen the oxidation curves show first an increasing and then a decreasing rate. A similar phenomenon has been observed by other investigators. Wagner and Grünewald²⁹ reported an initial period of increasing rate in the scaling of copper at high temperatures and low pressures. Bircumshaw and Preston²¹ found a marked "induction" period in the oxidation of

molten tin at low pressures. This effect of pressure may be associated with a change in the stability of the oxide nuclei and hence with a change in the rate of nucleation; Johnson and Mehl⁴⁴ have shown that curves of the shape indicated arise from processes of nucleation and growth. Thus, in spite of the greatly different nature of the metallic bases, and of the structure and rate of formation of the reaction products, the effect of low pressures in each of these cases was to change the nature of the initial reaction. While at high pressures the initial oxide forms apparently by an adsorption-diffusion process, at low pressures a process of nucleation and growth is operative.

SUMMARY

1. A sensitive method of thickness determination in the temper-color range of thicknesses was applied to a continuous study of the rate of oxidation of single crystals of copper at various temperatures and pressures for a number of crystal orientations.

2. The effect of surface preparation was investigated and a method giving reproducible surfaces was developed. Smooth surfaces were found to oxidize more slowly than rough surfaces at long oxidation times, more rapidly at short oxidation times.

3. The oxidation curves were of the form:

$$\frac{I}{l} = \frac{I}{a_1 e^{b_1 t}} + \frac{I}{a_2 e^{b_2 t}}$$

where t is time; l , thickness; e , the base of natural logarithms; and a_1 , a_2 , b_1 and b_2 , constants. Thus, when plotted on a logarithmic time scale, the oxidation curves consisted of two straight-line portions, the second being of greater slope.

4. The variation in oxidation rate with temperature was found to show a minimum in the constant $\frac{I}{b_1}$, for all crystal orientations with increasing oxidation temperature.

5. The orientation dependence of oxidation rate was found to be complex and to depend in general on angular distance from a singular direction at any one temperature and also to vary with temperature. The dependence could not be correlated with oxide-metal orientation.

6. The oxidation of iron crystals at 300°C. was also shown to obey the logarithmic equation.

7. With increasing oxygen pressure, the oxidation rate first increases to a maximum and then slowly decreases. The decrease was explained by an electron excess type of disordering in Cu_2O at low temperatures, and the increase by an expansion of the solid solution range of the oxide with increasing oxygen pressure.

8. The initial formation of the oxide on clean metal surfaces may be described as an adsorption-diffusion process at high pressures, and as a nucleation and growth process at low pressures. This was evidenced by a continuously decreasing oxidation rate with time at high pressures, and at low pressures by first an increasing, and later a decreasing, oxidation rate.

9. Similarities in the dependence of oxidation rate on time, temperature, crystal orientation, and surface preparation of iron, zinc, aluminum and copper were discussed in connection with a general theory of the oxidation of metals at low temperatures.

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DISCUSSION

(L. L. Wyman presiding)

U. R. EVANS,* Cambridge, England.—The authors' studies of the low-temperature oxidation of copper will be welcome, the more so as they bring out well the influence of crystallographic direction in determining the velocity—a factor that is shown qualitatively when microsections of polycrystalline copper or brass are heated, the different grains assuming different tints. I only propose to deal with one matter, on which the authors have quoted my opinion; namely, the use and limitations of interference colors as a guide to film thickness.

The interference color method has the undoubted attraction that it is possible to obtain "measurements without measuring." Never-

* Cambridge University.

theless, a very elementary insight into optical theory indicates that, in the form of the method that is sometimes employed, the measurements will be far from accurate. If, however, one cares to calibrate the color scale by some other method, it is possible to use interference colors to obtain values of reasonable accuracy. A favorable case is that of silver iodide films, which were studied by L. C. Bannister and myself 11 years ago.⁴⁵ Here five orders of colors can be obtained. Measurements of film thickness were carried out by three independent methods (microgravimetric, electrometric and nephelometric). It was found possible to employ all three methods on one and the same specimen, so that there was no question of "matching." Since good agreement between the three sets of measurements was obtained, it was fairly certain that the numbers were not far from the truth. Consequently, it was permissible to use any one of the methods for calibrating the color scale, and tables were constructed showing the range of thicknesses corresponding to the different tints. Some colors correspond to a very small range of thickness, and are thus a precise measure, whereas others represent an extensive range of thickness. It was found that the thicknesses calculated by the ordinary mode of employing interference tints were in many cases quite wrong.

It must be remembered that different methods of estimating film thickness do not necessarily measure the same thing. Most optical methods (certainly those depending on interference tints) measure the effective distance between two reflecting surfaces. In the case of interlocking between metal and oxide, for which there is much evidence today, a considerable amount of oxide might be buried away below the effective position of the lower surface, and not enter into the value obtained. The electrometric method gives only the oxide accessible to the cathodic action, which may not represent the whole. The gravimetric method gives the difference between the oxide present at the first and second weighings. If, as will usually be true, a sensible amount of oxide is present at the time of the first weighing, it may sometimes be necessary to estimate this by another method, and add it on, if it is

desired to have a measure of the total oxide present after heating.

Not many years ago, there were differences even in the order of magnitude between the thicknesses as found by different methods for the films corresponding to the various colors. This state of affairs was unsatisfactory. Today the values obtained by all the methods are found to give somewhat similar numbers, but discrepancies remain. These may be caused partly by methods that are insufficiently exact, but probably they are largely caused by the fact that different methods measure different things. If so, the differences between the results of different procedures, far from being a matter of dissatisfaction, add to our knowledge of the manner in which oxide and metal pass into one another. It is probable that several different methods ought to be used, before the true geometry of an oxidized surface can be fully understood.

W. H. J. VERNON,* Teddington, England.—I appreciate the opportunity afforded me of contributing to the discussion on this valuable paper, while regretting my inability at present to offer more than a few tentative comments on several of the many points raised. Primarily, I wish to offer my heartiest congratulations on the advance which this paper represents both in refinements of technique and in the conclusions to which it has led. The especial advantage of the authors' method, apart from its applicability to small single-crystal specimens, is its ability to give an almost continuous record of oxidation rate in the very earliest stages, which is just where the gravimetric method fails. It would be of great interest to see their results extended so as to fill the hiatus between and to correlate the two groups of results. On the question of methods of preparation, while I fully appreciate the fundamental value of the technique employed by the authors, I am inclined to doubt their surmise (p. 250) that "measurements on the . . . surface produced by abrasion should be of uncertain significance." If the abrasion is carefully conducted, quite a high degree of reproducibility can in fact be achieved; and, after all, the surface produced by abrasion cannot be left out of account in practical oxidation problems.

⁴⁵ U. R. Evans and L. C. Bannister: *Proc. Roy. Soc.* (1929) **125-A**, 370.

* Chemical Research Laboratory, Department of Scientific and Industrial Research.

The application of the logarithmic law to the low-temperature oxidation of single crystals of copper, for temperatures up to 155°C. , is of considerable interest. From gravimetric results (using ordinary polycrystalline surfaces prepared by abrasion) it was concluded^{46,47} that copper obeys the parabolic law at temperatures as low as 75°C. (possibly 50°C.). Is this overlap to be attributed to the different physical condition of the specimens, or is it essentially a question of time—the shorter the initial period over which the observations are made, the higher being the temperature at which the logarithmic relationship persists? Similarly with iron. Gravimetric results from ordinary abraded surfaces showed that the logarithmic law changed over to the parabolic law when a fairly well defined transition temperature, about 200°C. , was exceeded.^{48,49} On the other hand, for single crystals and short periods of exposure the authors have obtained logarithmic curves at 300°C. , while the transition temperature under their conditions may obviously be higher still.

Experiments with zinc⁴⁹ have suggested that the first-formed oxide is amorphous. Is it possible that this is generally true where the logarithmic law is followed? The question is difficult to answer experimentally, having regard to the small amount of oxide formed during such short periods at low temperatures, but the authors' views on this matter would be welcomed. A further interesting question relates to interference colors. It seems now to be fairly certain that the development of the usual sequence of colors is characteristically associated with the parabolic type of oxidation—e.g., copper over a wide temperature range, iron above 200°C. —and the absence of such colors with the logarithmic type—e.g., iron below 200°C. ,* zinc over a wide temperature range. In the light of the authors' results, copper at low temperatures is now seen to follow the logarithmic type; the absence of interference colors, at least at ordinary room

temperature, notwithstanding that the film may reach thicknesses well within the interference-color range for higher temperatures, I can confirm from my own early work.⁴⁷ These related groups of phenomena are possibly associated with a continuous type of film for the parabola and a discrete type—originating with an initial point-to-point attack—for the logarithmic curve; for example, microscopic examination of the oxide film on zinc shows very clearly a finely granular structure, in contrast with the continuous film on copper at the higher temperatures. The authors' work should throw considerable light on this question, and their conclusions will be awaited with interest.

D. ROSENTHAL,* Brussels, Belgium.—I should like first to express my deep appreciation to the authors for having given such conclusive evidence that no simple diffusion law can explain the process of oxidation of copper at low temperatures. Similar experiments have been performed by Mr. Lucaisi and myself at the University of Brussels. We have examined samples by means of electron diffraction in a device designed by Professor Finch, of the Imperial College of Technology, at London.

Our samples were of electrolytic copper and they were given the usual metallographic polishing. They were heated in vacuum up to 900° , then they were examined by the diffraction X-ray method. We found that the superficial layer was still in an amorphous state, as always after polishing. Despite very prolonged and very high-temperature annealing, the amorphous layer could not be removed; it could be removed only by etching, but we have found that etching renders more difficult the subsequent examination of oxide layers.

When subjected to oxidation at 200°C. , samples yielded after 3 min. a layer whose structure was the usual structure of cuprous oxide, but the size of the unit cell was 10 per cent greater, as was to be expected. We made the assumption that oxygen atoms are in solid solution in cuprous oxide and this would account for the increase of the unit cell.

Examination of samples after more prolonged heating, 1 hr. and up to 48 hr., showed progressive changes in the structures. The cuprous

⁴⁶ W. H. J. Vernon: *Jnl. Chem. Soc.* (1926) 2273.

⁴⁷ W. H. J. Vernon: *Trans. Faraday Soc.* (1927) 23, 117.

⁴⁸ W. H. J. Vernon: *Ibid.* (1935) 31, 1668.

⁴⁹ W. H. J. Vernon, E. I. Akeroyd and E. G. Stroud: *Jnl. Inst. Metals* (1939) 65, 301.

* This refers to ordinary polycrystalline surfaces prepared by abrasion. Mehl and McCandless [*Trans. A.I.M.E.* (1937) 125, 531] have, however, observed colors down to 140° on single-crystal specimens prepared by "hydrogen-etching."

* Chef de Travaux et Agrégé de L'Université de Bruxelles.

oxide type of structure had entirely disappeared and had been replaced by a very indefinite structure. The image was very poor and the lines very diffused, but after more prolonged heating the so-called cupric (CuO prime structure) appeared and then it was replaced by the regular CuO structure. A sample treated in the same way and oxidized for only 3 min. at 300°C . gave at once the structure CuO prime. We believe that if we could have performed the oxidation at lower temperatures—for instance, under 50°C .—like those used by the authors of the present paper, we would have been able to check perhaps the modification of the Cu_2O structures. I mean that perhaps we could account for the increase in the size of the unit cell.

It must now be said that the observed structure applies only to the superficial layer, since electron diffraction accounts for only 50 to 100 Å. thickness and ignores totally what happens in the layer that is below. Taking all this into account, we have now a very fair explanation of why a simple diffusion law cannot explain the oxidation of copper at low temperatures.

J. B. AUSTIN,* Kearny, N. J.—This paper is very interesting because it represents an application of the polarographic method, which has been rather too much neglected. It is a powerful tool and should be used far more than it has been.

Another point of interest is the effect of the roughness of the surface on the rate of oxidation. We have been making some measurements of the rate of oxidation of iron and steels at high temperature and have found that in this case the roughness of the surface has a very pronounced effect on the initial rate of oxidation at 1100°F . The difference between a milled surface, a pickled surface and a polished surface is noticeable, the milled surface oxidizing most rapidly and the polished surface least rapidly. This effect of the condition of the surface on the rate of oxidation has not been given as much attention as it deserves.

S. L. HOYT,† Columbus, Ohio.—In a study that I happened to make in this connection I was interested in the rate of oxidation of a

copper surface. The only thing of importance that seems worth mentioning here is that the particular experiment that I was running seemed to be interfered with by the evolution of gas from the copper sample. The method used was extremely sensitive to changes in pressure from this source.

In view of the anomaly reported by the authors at temperatures between 105° and 130°C ., it seems possible that the evolution of gas from the sample may have played some part. If the authors were studying the formation of scale, I do not believe this effect would have any bearing, but with a film of quite small thickness, the evolution of various gases, nitrogen, carbon monoxide, hydrogen and so forth, might in some way interfere with the normal diffusion of oxygen through this film of copper oxide, and in that way alter the rate at which the film forms.

The evolution of gas from the sample would be, of course, a temperature function and in that way would give two temperature functions, one of evolution of gas and the other of film formation. This suggests the use in these experiments of a thoroughly degasified sample of copper.

B. LUSTMAN AND R. F. MEHL (authors' reply).—As Dr. Evans states, all methods of determining film thickness by optical reflection from a film-covered metal surface (including that used in the present investigation) measure the distance between the film-gas and film-metal interface. In the method of surface preparation employed here, where smooth, single-crystalline, pure copper was used, the amount of "interlocking" or of internal oxide should be very slight, if not nonexistent.

While certainly, as Dr. Vernon points out, studies on the rate of oxidation of rough abraded surfaces are of considerable practical interest, it was felt that a full understanding of the external oxidation process would require studies in the first instance on surfaces as ideally smooth as possible.

The change-over from the logarithmic equation to the parabolic equation may well vary with the manner of surface preparation. It would be of interest to determine whether there is a transition temperature for the change-over from the one equation to the other or whether this occurs at a transition film thickness.

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It seems very doubtful indeed that the first-formed oxide on copper is amorphous; the fact that a well-defined orientation relationship exists between oxide and metal even when the former is very thick⁵⁰ would seem to disprove this contention conclusively, for surely an amorphous layer of only a few atoms in thickness would be sufficient to prevent an orientation relationship since the force field of an atom is inappreciable beyond a few atoms diameters. It would, furthermore, seem unlikely that the oxide film would be discontinuous and granular on the smooth, strain-free surfaces used in these experiments; such a film is more to be expected on severely stressed, abraded surfaces. It should also be said that brilliant interference tints were obtained on copper and iron through the range of logarithmic oxidation. The appearance of interference tints would seem to be correlated more with surface geometry than with manner of oxidation.

In reply to Dr. Rosenthal's discussion, it seems to us very unlikely that an amorphous layer (in the usual sense of this term) could remain on the copper surface after annealing at a temperature of 900°C. The reasoning

applied above to the suggestion that the oxide may be amorphous may be applied here also. It would seem more likely that the surface has become exceedingly smooth after this treatment; the halo diffraction pattern characteristic of amorphous surfaces may result on reflection from very smooth surfaces.^{51,52} While we agree with Dr. Rosenthal's statement that simple diffusion laws will not explain the course of oxidation of copper, we doubt, for the reasons stated in the paper, that measurable changes of phase in the film can account for the results obtained.

It is gratifying to learn that Dr. Austin observed an effect of surface geometry in the scaling of steel similar to that noted here in the rate of oxide-film formation on copper.

Pretreatment of the copper specimens both in a vacuum and in a purified hydrogen atmosphere were attempted and the oxidation rates in both cases were very similar. It would thus appear doubtful that, as Dr. Hoyt suggests, evolution of gases from the metal played an important role in determining the oxidation rates obtained.

⁵⁰ R. F. Mehl, E. H. McCandless and F. N. Rhines: *Nature* (1934) 134, 1009.

⁵¹ F. Kuchner: *Nature* (1932) 129, 545.

⁵² L. H. Germer: *Phys. Rev.* (1933) 43, 724.

Preparation and Some Properties of High-purity Copper

By J. S. SMART, JR.,* A. A. SMITH, JR.,* AND A. J. PHILLIPS*

(New York Meeting, February 1941)

THE preparation of a sufficient quantity of high-purity copper for extensive laboratory use in the study of impurity effects has been an integral part of a research program in progress at the Central Research Laboratory of the American Smelting and Refining Co. for the past several years. Initially the degree of purity desired was that necessary to meet two essential requirements for experimental accuracy: (1) no impurity was to be present in the copper in an amount capable of producing a detectable effect on the properties to be studied, (2) even the minor changes in properties caused by the addition of extremely small amounts of individual elements were to be measured without significant interference from contaminants. In the course of the investigation, evidence has accumulated to justify the conclusion that this copper is of exceptional purity; in fact, no impurity can be detected by any chemical method or spectrographic technique known to the authors. The present paper describes the method of production of the copper and presents some of its properties.

PREPARATION OF HIGH-PURITY COPPER

The elimination of impurities from commercial electrolytic copper is accomplished by a three-step purification process. The first operation consists of an electrolysis through a purified $\text{CuSO}_4\text{-H}_2\text{SO}_4$ electrolyte using bagged anodes, low current density (5 amp. per sq. ft.) and low tem-

perature (25°C. max.). The electrolyte is prepared from commercial Cu_2SO_4 and is purified by heating the solution and adding 1 gram Fe as $\text{Fe}_2(\text{SO}_4)_3$ to each 100 grams dissolved copper; sufficient hydrated oxide of copper, prepared from Cu_2SO_4 and NaOH, is supplied to precipitate $\text{Fe}(\text{OH})_3$, which carries down arsenic, antimony, tin, selenium, tellurium and other minor constituents. Silver and remaining traces of lead are removed by addition of Na_2S to the acidified filtrate, which is then refiltered after standing hot overnight. The cold solution is made up to 30 grams per liter Cu and 150 grams per liter H_2SO_4 and introduced without addition agents into the electrolytic system, which consists of a double row of hard-rubber battery boxes with the inside webbing and partitions removed, arranged in seven steps of ascending height. Electrolyte is uniformly supplied to the two highest cells by glass siphons operating from a constant-level reservoir, and flows by gravity through the bank of seven cells, entering each at the bottom and leaving at the top. Glass air lifts continuously supply the returning liquid to the constant-level reservoir for recirculation.

Each cell contains three $4\frac{3}{4}$ by $4\frac{3}{8}$ by 1-in anodes cast from high-quality electrolytic wirebar copper, various lots of which have been used with equal success. The anodes are pinned to sheet copper hangars shaped to prevent crawl of the electrolyte to the multiple-wired bus bars—which would result in fouling of the contacts—and hang inside wool flannel bags stretched over open wood frames. The deposit

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is obtained on starting sheets previously stripped from uncoated stainless-steel blanks; the finished cathode weighs about 5 lb. All impurities are satisfactorily removed except sulphur, which is present in the form of entrapped sulphates.

Despite certain disadvantages, oxidation by blowing the molten metal has proved the most satisfactory method for removal of sulphur. Thirty-pound melts are surface-blown to an oxygen content of about 1.5 per cent in a clay-graphite crucible heated by induction. Contamination of the melt by clay, iron and graphite is unavoidable, but the sulphur content is uniformly reduced below the limit of qualitative detection by conversion to H_2S and absorption in CdCl_2 solution. This degree of sulphur elimination is essential, since it is not completely removed by the subsequent processes. The melt is cast in the form of anodes, which are then re-electrolyzed through a high-purity $\text{Cu}(\text{NO}_3)_2$ solution to remove the contaminants picked up in the blowing operation. This electrolysis is carried out in glass cells at room temperature, using a current density of 15 amp. per sq. ft. The anodes are of the previously described dimensions and the starting sheets are likewise deposited in the apparatus on stainless-steel blanks. The electrolyte is made from pure copper and HNO_3 and is periodically purified by addition of a large excess of NH_4OH to precipitate the accumulated iron. After filtration, sufficient HNO_3 is added to precipitate most of the copper at pH 4, and the precipitate is washed by decantation to eliminate the bulk of the NH_4NO_3 . A minimum of HNO_3 is used to redissolve the precipitate, which is then diluted to 25 grams per liter Cu and used without further treatment at a pH of 2. The final deposit is bright, dense and very pure except for nitrates, which are eliminated by subsequent melting.

Inasmuch as the experimental work is generally performed on drawn wires, the

final manipulations involve the production of an oxygen-free pure copper rod suitable for drawing. Fortunately, surface contamination from steel tools and other

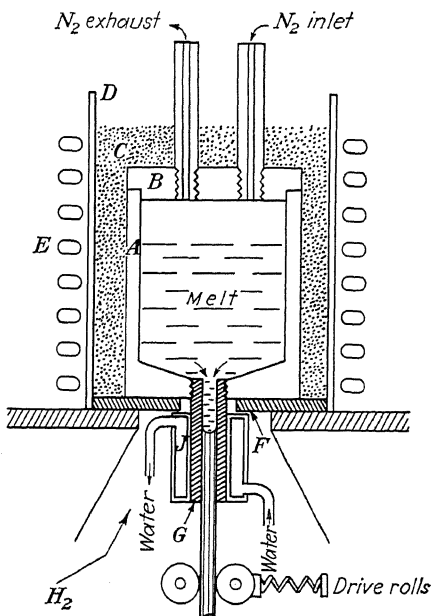


FIG. 1.—SECTION OF LABORATORY CONTINUOUS CASTING APPARATUS.

similar sources can be removed by pickling in HNO_3 , followed by hot 1:1 HCl , a precaution that is observed prior to all melting operations. The choice of a crucible that introduces no impurities into the melt and is adaptable to the production of oxygen-free castings is of great importance. Most crucibles contain either iron or sulphur in objectionable amounts, or are too porous. A special high-purity grade of Acheson graphite is the only material known to possess the necessary properties. It is available in the form of 4-in. diam. electrodes, from which the desired crucibles are machined for each of the various melting operations. Oxygen-bearing melts may be readily cast from an open crucible by pouring through air into a mold of the same material. Pure oxygen-free copper and its alloys are cast in the form of

smooth, dense $\frac{3}{8}$ -in. rod by a continuous casting process in which the cooling is effected laterally.

Fig. 1 represents a diagrammatic cross section of the necessary apparatus. A previously prepared 10-lb. oxygen-bearing pure copper slug is accommodated by crucible *A*, which rests on insulating ring *F*. Tight-fitting cover *B* is provided with pure graphite tubes for the inlet and exhaust of purified nitrogen sweeping gas, the whole being packed in tamped lamp-black *C* retained by silica sleeve *D*. The graphite casting die *G* is threaded through the bottom of the crucible and is encased in a water jacket *J*, which extracts practically all of the heat laterally through the copper and die wall. After the casting die is plugged with a pure copper "starting rod," which is held in position by the tension on the driving rolls, heat is supplied by means of a high-frequency coil *E*. The bottom of the crucible is protected from oxidation by a hydrogen pocket, and the melt is allowed to stand for about 30 min. while deoxidation and thorough mixing are accomplished. The nitrogen sweeping gas removes excess hydrogen to permit the production of high-density copper rod. The power-driven rolls automatically cast the melt at a uniform rate by continuous withdrawal of the solidified rod from the die.

This process is ideal for the elimination of oxygen, because both solidification of the melt and further cooling of the rod to a low temperature occur within an enclosed system where the copper is in contact at all times with only carbon, carbon monoxide, hydrogen and nitrogen. However, since strictly oxygen-free copper was considered essential, experimental verification of the efficiency of deoxidation was obtained by several methods. The evidence is necessarily of an indirect nature because the accepted method for analysis of oxygen is definitely known to be inaccurate for extremely small amounts, owing to a

variable adsorption of oxygen on the surface of the sample.¹ The addition of 0.00007 per cent Fe to pure copper resulted in a small but reproducible loss of conductivity, indicating that insufficient oxygen was present to remove this amount of iron from solid solution by formation of an insoluble oxide. According to Rhines,² the composition of the oxide is Fe_3O_4 . If it is assumed that the quantity of dissolved oxygen in equilibrium with solute iron is negligible, the presence of only 0.000027 per cent O_2 would have completely precipitated the iron and eliminated the conductivity drop. Another and more striking example of the extent of deoxidation was supplied by adding SiO_2 to a charge of pure copper, which was then melted and continuous cast in the usual way. Reduction of SiO_2 was effected, the silicon entering solid solution to form an alloy. The same alloy removed traces of oxygen from commercial hydrogen at 850°C . by formation and precipitation of SiO_2 in the copper. Hydrogen, in turn, readily removes oxygen from pure copper at the same temperature.

The employment of the usual chemical methods for the detection of minute amounts of other impurities, especially those normally present in commercial copper, has proved generally unsatisfactory because of a lack of sensitivity. The spectrograph offers more attractive possibilities for work of this type, particularly when a high-arc current is used across suitable lengths of rod acting as self-electrodes. The limits of visibility have been explored on alloys prepared by synthesis from pure copper and various master alloys. Despite the excellent sensitivity of the method, no impurity is detectable in the cast oxygen-free pure copper rod. Although a precise statement with regard to specific purity is not possible at the present time, it is certain that the minimum copper content is 99.999 per cent.

¹ References are at the end of the paper.

Column II of Table I lists the composition of binary alloys of pure copper and the common impurities. Each of the impurity contents noted is detectable spectrographically and represents a definite excess over the quantity present in pure copper. Most of the compositions given in that column do not correspond to the low limits of spectrographic detection that have been conservatively estimated from the line gradients and listed in column III. In all probability the amount of each impurity present in the pure copper is indeterminately lower than that represented in the latter column.

TABLE I.—*Impurity Limits in Continuous Cast High-purity Copper Rod*
PER CENT BY WEIGHT

| I Element | II Definite | III Probable | IV Method |
|--------------|----------------|-----------------|-----------------------|
| Fe | <0.00007 | <0.00005 | Spectrographic |
| Sb | <0.0001 | <0.0001 | Spectrographic |
| Pb | <0.0001 | <0.00005 | Spectrographic |
| Sn | <0.0001 | <0.00005 | Spectrographic |
| Ni | <0.0001 | <0.0001 | Spectrographic |
| Bi | <0.00001 | <0.00001 | Spectrographic |
| Ag | <0.00003 | <0.000001 | Spectrographic |
| As | <0.0002 | <0.0001 | Spectrographic |
| Cr | <0.00005 | <0.00001 | Spectrographic |
| Si | <0.00001 | <0.000001 | Spectrographic |
| Te | <0.0002 | <0.0001 | Spectrographic |
| Se | <0.0001 | | Chemical, 500 grams |
| S | <0.0001 | | Chemical ^a |

^a Checked by E. N. Skinner, Jr. Unpublished Thesis to Faculty of Yale University, May 1940.

From the description of the casting method, it is apparent that several other elements are in close contact with the melt and should receive consideration as contaminants; viz., C, CO, N₂ and H₂. The solubility of carbon monoxide in solid copper has been demonstrated to be of a negligible order, by Sieverts and Krumbhaar,³ Röntgen and Müller,⁴ Allen,⁵ and Ransley.⁶ This, however, does not preclude lack of solubility on the part of carbon, although the possibilities are decidedly limited theoretically. If for the moment a small solubility is assumed, which is in all probability dependent on temperature, changes in certain properties would be expected from various heat-treatments

designed to produce the solubility extremes. The results of experimental exploration of these possibilities have been entirely negative. Furthermore, the addition of oxygen should prove beneficial (as previously described for iron) if carbon is present in sufficient amounts to affect the properties, and this is not true.

Hydrogen is undoubtedly present in the cast rod, and the quantity in solution is at least partly dependent on the efficiency of the previously described nitrogen sweep. Although vacuum removal has not been attempted, samples of the rods have been surface-oxidized in air at 850°C. and heated at this temperature in an atmosphere of pure dry nitrogen for periods as long as 21 days. This treatment should result in a substantial diminution of the hydrogen content for comparison with other samples that were saturated with hydrogen at the same temperature. Köster⁷ extracted hydrogen from several types of copper at elevated temperatures, cold-worked the samples, and found a substantial decrease in the temperature at which softening occurred as compared to the original untreated material. However, none of the pure copper samples prepared as above exhibited any trace of this effect; the values obtained for the original cast rod, the oxidized and nitrogen-swept rod, and the hydrogen-saturated rod all agreed within the limits of accuracy of the method. It is the authors' opinion that the changes in properties noted by Köster were due to variations in the solubility of impurities other than hydrogen, resulting from the thermal treatment involved in the vacuum elimination. No evidence has been obtained to justify the proposition that hydrogen has an influence on the physical properties of pure copper in the solid state.

The many published accounts regarding the insolubility of nitrogen in both molten and solid copper will not be reviewed here. All of the present experimental observations confirm this generally accepted

premise. If a finite solid solubility of nitrogen in copper actually does exist its effect on the properties that have been studied is indeterminately small.

SOME PROPERTIES OF HIGH-PURITY COPPER

As cast, the $\frac{3}{8}$ -in. rod is very soft and evidently can withstand an unlimited amount of cold-working, but the grain size is undesirably coarse for many purposes, and a number of intermediate anneals are usually employed in the cold-drawing schedule to obtain refinement. Variations in the annealing temperature between 300° and 800°C. have a negligible influence on the properties investigated, exclusive of grain size and its related effects, as would be expected from a metal of high purity.

Conductivity

The conductivity of numerous lots of pure copper as determined by a standard Hoopes bridge over a period of several years averages 102.3 per cent of the I.A.C.S., corresponding to a resistivity of 0.14983 ohms per meter gram at 20°C. As would be expected from the experimental limits of error, the determinations vary between 102.25 and 102.35 per cent. Theoretically, oxygen present in solid solution should lower the conductivity of strictly pure copper, but its addition to impure copper invariably results in a conductivity increase due to removal of certain impurities from solid solution. The effect of soluble oxygen has been investigated by permitting various samples of oxygen-free rod to absorb oxygen by diffusion to the point of saturation at 850°C., and drawing test wires for measurement. Table 2 lists a number of determinations made on a standard Kelvin bridge, which indicate that oxygen does actually lower the conductivity to a very small extent. The oxygen-free samples were annealed in hydrogen at 500°C. and oxygen-bearing wires in nitrogen at 500° and 850°C. The samples in the form of straight lengths were immersed in

an oil bath of uniform temperature and the measurements were corrected to 20°C. by the usual method.

TABLE 2.—*Conductivity of Samples Annealed for One Hour at Indicated Temperatures and Cooled by Rapid Quenching*
PER CENT

| Sample No. ^a | Description | Conductivity, Per Cent | |
|-------------------------|---|------------------------|--------------------|
| | | Annealed at 500°C. | Annealed at 850°C. |
| A | Oxygen-free..... | 102.32 | |
| B | Oxygen-bearing (saturated at 850°C.)..... | 102.23 | 102.10 |
| C | Oxygen-bearing (check run)..... | 102.21 | 102.23 |
| D | Oxygen-free..... | 102.39 | |
| E | Oxygen-bearing..... | 102.19 | |

^a Samples D and E taken from the same wire as samples A and B were kindly measured by the investigators of another laboratory.

Because of the small magnitude of the loss of conductivity as measured from the wires annealed at 500°C., where the solubility of oxygen is considerably lower than at 850°C., the anneals at the higher temperature were included with the expectation of obtaining a larger difference. The data are inconclusive on this point, but the results cannot be definitely classified as anomalous because of lack of information on their approach to equilibrium conditions, and the limits of experimental accuracy. There is no disagreement, however, with respect to the existence of a loss of conductivity due to the presence of oxygen in solid solution.

Cold-working

The effects of cold-work on the mechanical properties of copper, and the factors influencing its annealing characteristics have been studied by numerous investigators. For the most part the data now available have been obtained from coppers of varying commercial composition, and since impurity effects are often of considerable magnitude, the variations in the properties

of high-purity copper when cold-worked and annealed under certain conditions are of general interest. Some effects of cold-working will be considered first, following

tested on a Scott wire tester of 50-lb. capacity at an indeterminate higher rate of strain, the minor disadvantages of which were more than overcome by the increased

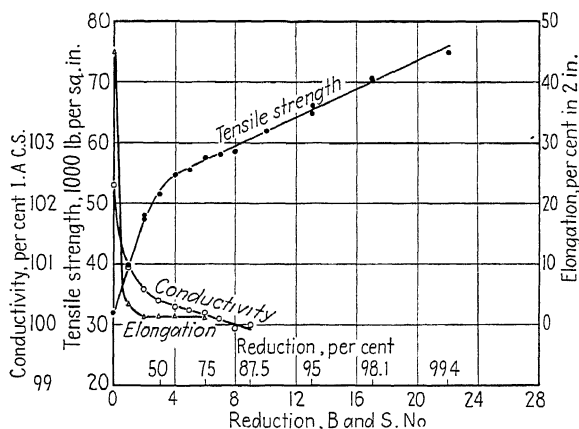


FIG. 2.—EFFECT OF COLD-DRAWING ON SOME PROPERTIES OF PURE COPPER.

which they will be compared with the changes accompanying annealing.

The cast structure of the $\frac{3}{8}$ -in. continuous cast rod was broken down by cold-drawing 30 per cent, 32 per cent and 37 per cent, employing an intermediate anneal of 30 min. at 600°C. in hydrogen after each of these reductions, to provide 0.204 in. (No. 4 B. and S.) annealed wire (0.07 mm. grain size) for the determination of the effect of deformation by cold-drawing on the tensile strength, elongation and contraction of area. The wire was then cold-drawn 22 B. and S. numbers on a string-up machine at a rate of 192 ft. per min., being coiled on a block of 17-in. diameter and cooled between dies. Test samples were taken after most of the die reductions, as permitted by the quantity of the wire.

Tensile strength and elongation were determined from wires of 10-in. gauge length; the diameters were measured by means of micrometers. For samples drawn up to 13 numbers, two recently calibrated hydraulic machines were used, which could be read to within 1.0 per cent of the applied load, using a rate of strain of 0.0125 in. per in. per min. The finer sizes were

sensitivity of load measurement. Elongation measurements were taken from divider settings, using small scratches on the specimens for reference markings. Because of the small size of the samples, the determinations of the contraction of area are subject to sufficient error to mask the small changes that occur during the cold-working of this very pure material, even though the fractures were magnified 50 \times and projected on a ground glass for evaluation. In general, a contraction of area of 94 per cent, representative of the annealed wire, dropped to about 92 per cent for samples drawn 14 numbers.

The conductivities of samples cold-drawn 0 to 9 numbers were also determined, each of the measurements being made on 0.081-in. diam. wire using a standard Hoopes bridge. These samples were drawn from a hot-rolled rod fabricated from an oxygen-free slug in such a way as to minimize exposure to air at high temperature, and consequent oxygen absorption. The rod was then drawn through the various sizes between 0.229 and 0.081 in. and a sample from each die reduction was annealed at 500°C. for 1 hr. This

procedure furnished a series of annealed wires of progressively increasing diameters, but of similar grain size (0.035 to 0.04 mm.), which when cold-drawn to 0.081 in. produced samples drawn 0 to 9 numbers hard.

The comparative effects of cold deformation by drawing on tensile strength, elongation and conductivity are represented in Fig. 2. By plotting the data against B. and S. numbers, each of which represents a reduction of slightly over 20 per cent of the cross-sectional area of the wire entering the die, the progressive effects of equal increments of reduction may be determined directly from the curves. Thus the first four reductions have large but steadily decreasing unit effects on the tensile strength, after which the relationship becomes linear for the next 14 numbers. At higher reductions a further decrease in the slope of the curve might be predicted on the basis of an appreciable increase in the tendency for self-annealing, but the small dimensions of the wires introduce errors of such magnitude as to preclude accurate determination of this possibility.

Alkins⁸ has described an arrest in the increase in tensile strength of hard-drawn copper, but has plotted his results against cross-sectional area, and the curve does not represent the effects of equal increments of cold reduction. Although the reduction at each stage of the drawing procedure was not the same for all of Alkins' test wires, the six samples that determined the arrest had been reduced 13.6 per cent per draft, with one exception of 12.6 per cent. When replotted against reduction numbers, these data did not indicate the presence of the arrest, but determined a straight line, the deviations being within the limits of error and of about the same order as the data of Fig. 2. A similar ambiguous effect is obtained by plotting tensile-strength data against total percentage reduction of area.⁹⁻¹¹

Of particular interest is the manner in which the various properties change with the degree of cold-working. Fig. 2 clearly indicates that elongation is the property first affected; the change occurs so early that the major part of the total decrease is obtained during the first die reduction. The next highest initial rate of change is to be found in the conductivity curve. Impurities, in small amounts, do not appear to have a significant effect on the total loss of conductivity caused by cold-working, since the average loss of a number of wirebar coppers drawn 9 numbers was 2.25 per cent as compared to the present drop of 2.3 per cent. Similarly, the tensile strength of annealed pure copper differs very little from that of the commercial product; both appear to vary between 31,000 and 32,000 lb. per sq. in. The rate of increase of the tensile strength, as determined by the first increments of cold-work, is decidedly smaller than the similar changes of opposite sign occurring in the elongation and conductivity.

One of the most interesting effects of cold deformation on the properties of copper is the well-known decrease in density obtained from wrought and annealed coppers that have been further cold-worked by any of several methods. Typical measurements of the density changes as functions of the degree and method of cold-working have been reported by Alkins¹⁰ and Maier.¹² In addition, there appears to be a discrepancy between the density of copper as determined directly and that calculated from X-ray measurements. Maier obtained a value of 8.95285 grams per c.c. at 20°C. from a single crystal, which is considerably higher than the calculated result of 8.9381 grams per c.c. tabulated by Stockdale¹³ from the X-ray determinations of Van Bergen¹⁴ and Roberts.¹⁵ Although the scope of the present paper does not permit a thorough study of these phenomena, it was thought advisable to include sufficient

data to indicate the behavior of pure copper when subjected to various treatments that might be expected to alter its density.

continuous cast rod were measured in the as-cast condition, and the remainder cold-drawn by the method previously described for further tests.

TABLE 3.—*Averaged Densities in Grams per Cubic Centimeter at 20°C.*

| Nominal Reduction, Per Cent ^a | Oxygen-free Pure Copper | | | Pure Copper +0.037 Per Cent O ₂ | Commercial Copper | | |
|---|-------------------------|------------------------|----------------------|--|---------------------------------------|---------------|--------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| | Single Crystal | Coarse Polycrystalline | Fine Polycrystalline | Fine Polycrystalline | Wirebar 0.041 Per Cent O ₂ | Allkins' Data | Maier's Data |
| 0 | 8.9577 | 8.9592 | 8.9581 | 8.9379 | 8.9314 | 8.9165 | 8.92426 |
| 50 | | 8.9560 | 8.9563 | 8.9304 | 8.9200 | 8.8918 | 8.90877 |
| 90 | | 8.9550 | 8.9548 | 8.9214 | 8.9226 | 8.8866 | 8.91052 |
| DIFFERENCES IN DENSITY CAUSED BY COLD-DRAWING | | | | | | | |
| 50 | | 0.0032 | 0.0018 | 0.0075 | 0.0114 | 0.0247 | 0.01549 |
| 90 | | 0.0042 | 0.0033 | 0.0105 | 0.0088 | 0.0299 | 0.01374 |

^a Actual reductions for rod No. 2 were 50.5 and 90.2 per cent; for Nos. 3 to 5, 49.8 and 90.0 per cent; for No. 6, 47.29 and 89.76 per cent; for No. 7, 53.37 and 90.53 per cent.

The effects of grain size and several degrees of deformation were determined from pure copper in the oxygen-free condition, and compared with the results obtained from pure copper and a typical sample of commercial electrolytic copper of wirebar grade, both of which contained excess oxygen in the form of cuprous oxide. A single crystal of pure copper was measured in the cast condition but unfortunately was not large enough for deformation by drawing. Polycrystalline material continuously cast from the same lot provided samples having a large grain size, while hot-rolled pure copper rod furnished the fine-grained condition. The latter sample was hot-rolled from an oxygen-free slug by the previously noted method of short exposure to air at high temperature. The oxygen-bearing pure copper rod was hot-rolled from a cast slug, and the commercial sample from a wirebar slice. All hot-rolled rods were drawn from 0.3125 to 0.257-in. diameter and annealed 1 hr. at 600°C. to furnish annealed samples for measurement and further cold-working. Portions of the

Density measurements were made on carefully cleaned portions cut from each end of the annealed or cast rods and on samples from the remaining sections after cold-drawing 50 and 90 per cent. The method employed is similar in principle to that described by Maier. Samples of 15 to 50 grams were weighed on a large analytical balance sensitive to ± 0.0001 grams, and then in C.P. CCl₄, in which they were suspended by means of a fine platinum wire. A temperature-density curve for the CCl₄ was constructed by use of a picnometer, which in turn was calibrated against mercury. The CCl₄ was contained in a glass flask of 500-ml. capacity, equipped with a cork that admitted the wire through a small glass tube. The volume of the flask was large enough so that by stirring immediately prior to weighing, and suspending the sample in the center of the container, temperature gradients were eliminated within the limits of sensitivity of the thermometer, which could easily be read to 0.05°C. The same thermometer was used for all measure-

ments, including the determination of the density of the CCl_4 , and occupied a position immediately adjacent to the specimen in the flask. As a precaution, the apparatus was generally allowed to remain undisturbed for a sufficient period of time after the initial weighing to ensure a change in temperature, then a second reading was made; the checks were always within, and generally much better than 5 parts per 100,000. After appropriate deductions for the suspension wire, the measurements were corrected to 20°C . on the basis of a volume coefficient of expansion for copper of $3 \times 16.8 \times 10^{-6}$ per degree centigrade. The accuracy of the method is conservatively estimated as 1 part in 10,000. The results are listed in Table 3.

It is evident that the densities obtained from the oxygen-free pure coppers are somewhat higher than Maier's results for a single crystal, and that the order of the discrepancy between these values and that calculated from lattice-parameter measurements is far too large to be dismissed as an error in the experimental measurements. Since the density of the single crystal is slightly lower than the polycrystalline cast rod made from the same lot, and approximately equal to that of the hot-rolled rod, it is most probable that grain size has such a small effect on density that its determination is beyond the accuracy of the present method, including the variation in density encountered in the preparation of the samples as part of the error.

The decreases in the densities of the two oxygen-free pure coppers after reduction of 50 and 90 per cent are of a very small order by comparison with those encountered in commercial coppers, as found in the present investigation, and by Alkins and Maier. The aspects of the entire phenomenon have been so altered, in fact, that it is even doubtful whether pure copper actually does suffer a decrease in density during cold-working. It is freely admitted

that the present data do no more than suggest this possibility. Its proof is quite another matter, involving some advanced investigation of the effects of the increased surface produced by deformation on the accuracy of the determinations, and an extremely careful research.

The addition of 0.037 per cent O_2 to pure copper resulted in a loss in density in the annealed condition, which, curiously enough, is greater than the effect calculated from the density of cuprous oxide. Furthermore, a subsequent loss due to cold-working was obtained, and its magnitude leaves little doubt that cuprous oxide is an important contributor to this phenomenon, possibly by giving rise to the formation of minute internal voids. There is considerable variation in the behavior of the oxygen-bearing coppers with reference to the relationship between density loss and percentage of reduction, but impurity effects must receive consideration, and in addition, Alkins and Maier have indicated the existence of a minimum in the curve.

Annealing Characteristics

The large influence of impurities on the softening temperature of copper is well known, and there is little question that the thermal history prior to cold deformation is also an important consideration if impurities are present. High-purity copper therefore greatly facilitates the acquisition of fundamental data concerning the effects of three important variables—deformation, annealing time and annealing temperature. According to Tammann,¹⁶ the restoration of certain properties during annealing is a simultaneous process for copper, but since it has been shown that the changes occur in a definite sequence during cold drawing, it is also of interest to compare the results of annealing from this standpoint.

The necessary data were secured from a 10-lb. coil of $\frac{3}{8}$ -in. oxygen-free continuous cast rod. In order to obtain a series of samples reduced 50 per cent, 75 per cent

and 87.5 per cent by cold-drawing, but of 0.081-in. dia. finished gauge, the break-down drawing and annealing cycles neces-

per cent, annealed for 1 hr. at 140°C. and tested in tension. Their tensile strengths agreed within 1000 lb. per sq. in. which,

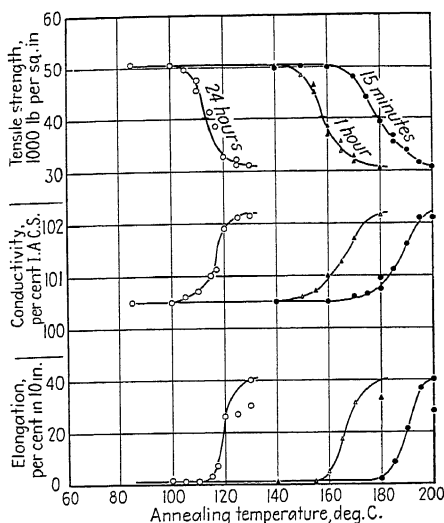


FIG. 3.—ANNEALING CHARACTERISTICS OF PURE COPPER WIRE REDUCED 50 PER CENT.

sarily differed for each series, and are given in abbreviated form:

50 Per Cent Series: reductions of 53.5 per cent, 37 per cent, 37 per cent and 37 per cent, each followed by an anneal for 30 min. at 600°C. Finish-drawn 50 per cent to 0.081 inch.

75 Per Cent Series: reductions of 30 per cent, 32 per cent, 37 per cent and 37 per cent, each followed by an anneal for 30 min. at 600°C. Finish-drawn 75 per cent to 0.081 inch.

87.5 Per Cent Series: reductions of 40.5 per cent and 37.5 per cent, each followed by an anneal for 30 min. at 600°C. Finish-drawn 87.5 per cent to 0.081 inch.

After the final intermediate anneal, small samples of each of the various rods were tested for uniformity with respect to their response to a standard annealing treatment to ensure freedom from such variations as might have been produced by the differences in the break-down procedures. For this purpose the samples were reduced 75

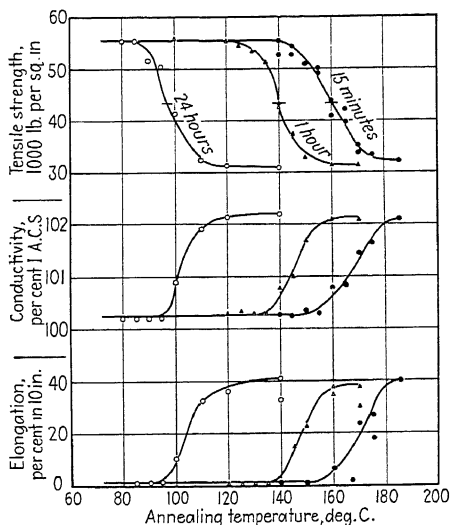


FIG. 4.—ANNEALING CHARACTERISTICS OF PURE COPPER WIRE REDUCED 75 PER CENT.

from Fig. 4, will be seen to be well within the limit of reproducibility for check wires subjected to this treatment. Following this justification of the method of preparation, the processed wires were drawn to test size and cut to lengths of 1 meter each. Samples were then annealed in two automatically controlled oil baths, one for temperatures below 130°C., in which the maximum variation was $\pm 0.25^\circ\text{C}$., the other for higher temperatures within limits of $\pm 0.5^\circ\text{C}$. For each of the three reductions, three annealing periods were used—15 min., 1 hr. and 24 hr. Conductivities were determined on a Hoopes bridge, following which the wires were cut in half to furnish check samples for the tensile test. The annealing curves are plotted in Figs. 3, 4 and 5.

It is evident that during annealing the changes in tensile strength, conductivity and elongation do not proceed simultaneously, but in a sequence which is the reverse of that occurring during cold-working. A

comparison of the curves for the 1-hr. anneals of Fig. 4, along the 140°C. vertical, illustrates a 50 per cent loss of work-hardening as measured by tensile strength,

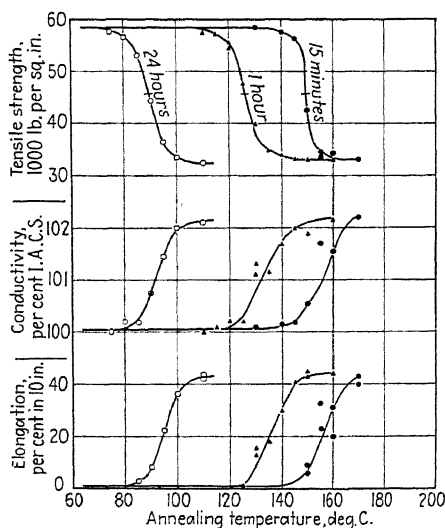


FIG. 5.—ANNEALING CHARACTERISTICS OF PURE COPPER WIRE REDUCED 87.5 PER CENT.

a much smaller restoration of conductivity, and the appearance of but a slight increase in elongation. Additional comparisons prove the generality of this effect.

By inspection of the tensile-strength curves, the effects of reduction, time at annealing temperature, and the general temperature range over which recrystallization occurs are self-evident. However, it is often of considerable convenience to express the softening process in terms of a definite softening temperature, for comparative purposes. This generally involves the determination of a portion of the annealing curve by adoption of a standard reduction and annealing time, and the selection of some point on the curve, such as the beginning of the process or the end of the process, from which the desired temperature may be read. A procedure that depends on the determination of the half-hard point has several features to

recommend its selection.* Variations in the tensile strength between various coppers given equal cold reductions, and differences in the temperature range over which softening occurs, are accounted for, and good accuracy is ensured by the large slope of the curve as it passes through this range.

The half-hard stages of the curves of Figs. 3 to 5, as determined from the plotted annealing data, are designated by the small horizontal lines. For example, detectable softening of pure copper cold-drawn 87.5 per cent and annealed for 24 hr. first appears at about 75°C., is complete at about 110°C., and the softening temperature is 89°C. It is of some interest to note the differences in softening temperature caused by variations in the annealing time (Table 4).

Allowing for the limited scope of the data, which does not permit generalization, it appears that the effect of annealing time is reasonably free from dependence on reduction for the particular reductions investigated. In addition, the data fit the general rule that a decrease in softening temperature of 10°C. is obtained by doubling the annealing period.

TABLE 4.—Decrease in Softening Temperature Due to Indicated Variations in Annealing Time
DEGREES CENTIGRADE

| Reduction, Per Cent | 15 Min to 1 Hr. | 15 Min to 24 Hr |
|------------------------|-----------------|-----------------|
| 50 | 21 | 66 |
| 75 | 20 | 62 |
| 87.5 | 21 | 60 |

SUMMARY

1. High-purity copper of a minimum purity of 99.999 per cent Cu has been

* The method extensively used by the authors over a period of several years for many different types of copper has proved thoroughly reliable. The sample to be investigated is reduced 75 per cent by drawing and its tensile strength is determined in this, the "hard" condition. The annealed tensile strength is obtained from a 1-hr. anneal at 500°C.; these extremes determine the half-hard point. A sufficient number of 1-hr. anneals at suitable temperatures provide the data necessary to plot the portion of the curve passing through the half-hard range, and the softening temperature is obtained graphically. In most cases the reproducibility of the method is $\pm 2^\circ\text{C}$.

prepared in sufficient quantity for extensive use as a research material.

2. The resistivity of oxygen-free high-purity copper is 0.14983 ohm per meter gram at 20°C., corresponding to a conductivity of 102.3 per cent of the I.A.C.S.

3. The presence of oxygen in solid solution in pure copper increases its resistivity by a small but measurable amount.

4. Data have been presented to indicate the changes in tensile strength, elongation and conductivity that occur when pure copper is progressively cold-worked by drawing.

5. The density of pure copper has been determined as 8.9592 grams per c.c. at 20°C.

6. The density changes that accompany the cold-working of oxygen-free pure copper are of a very small if not a negligible magnitude. When oxygen is present in the form of cuprous oxide, the decrease of density during cold-working is appreciable.

7. The changes in tensile strength, elongation and conductivity, of cold-worked pure copper annealed at various temperatures have been determined for three different degrees of reduction and annealing time.

ACKNOWLEDGMENT

The authors take great pleasure in expressing their indebtedness to Dr. R.D. McLellan, for assistance in the spectrographic analyses, and to Mr. Stephen Mikula, who prepared most of the samples and carried out a number of the mechanical tests.

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APPENDIX

An appendix, consisting of tables showing data of Fig. 2 and annealing data, has been issued as auxiliary publication, and may be obtained by writing to the American Documentation Institute, Offices of Science Service, 2101 Constitution Ave., Washington, D. C., asking for Document No. 1465 and remitting 27¢ for microfilm (images 1 inch high on standard 35-mm. motion picture film) or 90¢ for photoprint (readable without mechanical aid).

DISCUSSION

(E. M. Wise presiding)

W. M. BALDWIN, JR.,* Cleveland, Ohio.—The question was raised during the oral discussion to this paper whether there would have been some softening effect at room temperature suffered by the hard-drawn material between the time of preparation and time of testing. Some idea of the rate of softening at room temperature has been hinted at by the authors in the last three paragraphs of their paper. Their line of thought has here been extended. Fig. 6 has been constructed from the data contained in their Figs. 3, 4 and 5. The times and temperatures of the half-hard points of the tensile-strength curves of wire reduced 50, 75 and 87.5 per cent have been plotted, using the logarithm of the time and the reciprocal of the temperature. Straight lines result. Extrapolating the lines to room temperature (20°C.) shows that it would take almost 9 years for the most severely worked samples to reach the half-hard point at a room-temperature anneal and almost 60 years for the least severely worked samples to do the same. The slopes of the lines are seen to be the same in all three cases. Fitting these lines to the general equation:

$$A = A_0E - \frac{Q}{RT}$$

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outlined by Dushman,¹⁷ which in the logarithmic form

$$\log A = -\frac{Q}{RT} + \log A_0$$

the values of Q s derived from tensile-strength vs. temperature curves (around 6000 cal.), Dushman (loc. cit.) forwards the hypothesis that in the case of tensile-strength heats of

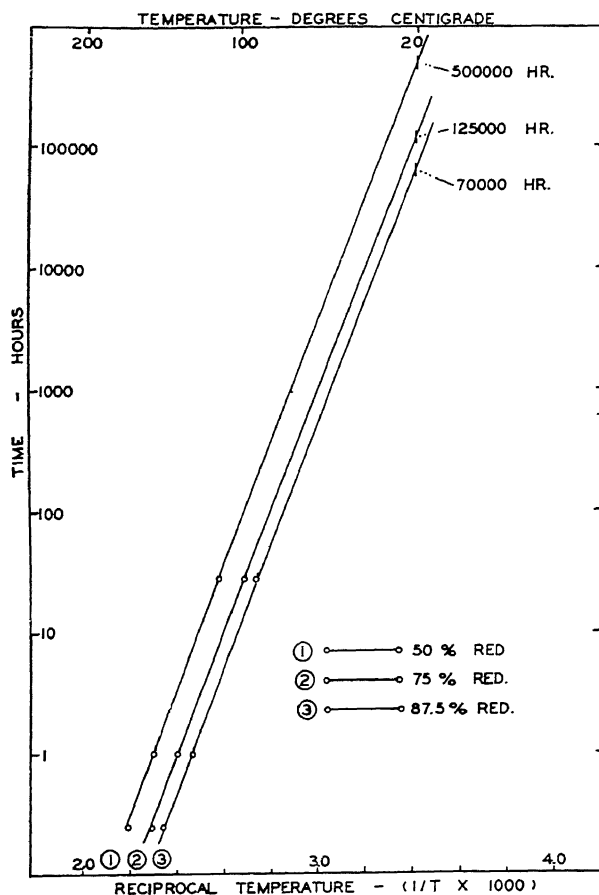


FIG. 6.

is of the straight-line form of

$$y = sx + b$$

where s , the slope, is represented by $-\frac{Q}{R}$, the values of Q (which, in this case, would be the energy of the annealing reaction) may be directly computed from the slope of the lines as being 22,900 calories.

This value lies below the values of the activation energy for copper computed from self-diffusion data (around 60,000 cal.) and above

reaction "the reaction involved is either a motion of relatively large units, such as the grains, or a motion of similar atoms past each other; the reaction in diffusion is one in which individual atoms of one kind have to interchange places with atoms of another kind." The fact that the present value of heat of reactions lies midway between the two values discussed by Dushman may indicate that the size of unit involved in the softening process is between the sizes involved in the diffusion and tensile strength processes.

¹⁷ S. Dushman: *Proc. Amer. Soc. Test. Mat.* (1929) 29, 7.

S. SKOWRONSKI,* Perth Amboy, N. J.—The staff of the Research Department of the American Smelting and Refining Co. is to be congratulated; first, on the production of what may be called Chemically Pure Copper and second, on the work now being done on the physical properties of this super pure copper. A great deal of the discrepancy in the literature regarding the properties of copper arises from the fact that the experimenters used different types of copper with varying chemical composition, and with a source of pure copper now available we should be able to obtain more consistent results and better fundamental data.

E. M. WISE,† Bayonne, N. J.—Have the authors studied the recrystallizing behavior of this extremely pure material at low reduction, of the order of perhaps 5 to 25 per cent?

I ask because of some work that we did on platinum of very high purity. It appeared that the grain size of this material was determined almost wholly by the reduction, and the material was very reluctant to grow grains.

J. CHIPMAN,‡ Cambridge, Mass.—I want to report a finding that may have some bearing on the purity of this copper, and to ask whether the authors have any evidence along the same line.

The porosity of copper cast in certain atmospheres may be explained if carbon is slightly soluble in liquid copper. To test this idea, Mr. Leonard, in our laboratories, melted copper in an atmosphere of nitrogen in an Acheson graphite crucible, pouring the copper through a hole in the bottom of the crucible directly into a tank of water. Then we analyzed the copper for carbon by the same combustion method that we use for low-carbon steel, and with very careful analysis we found what might be reported as a trace of carbon in the copper. The amount found did not appear to depend upon the melting temperature, and was always small; it would average 0.003 per cent, which is more than the experimental errors of the analysis.

Since the highly purified copper reported in this paper was also melted in graphite, it may have contained a similar proportion of carbon.

It seems altogether possible, therefore, that the amount of this impurity may be three times as great as the sum of all the others. This would not necessarily be evidenced by conductivity data, since, as the authors point out, the solubility of carbon in solid copper is probably exceedingly small.

C. S. SMITH,* Waterbury, Conn.—Have the authors noted any change in property or structure of their high-purity copper at room temperature after cold-working? Particularly, it would be interesting to know whether any change occurred during cold-drawing or in the interval between cold-drawing and annealing.

Persons not connected with the copper industry should be cautioned that the conductivities given in the paper are mass conductivities based on measurement of resistance, length and weight, not cross-sectional area. The density of pure copper—indeed, even of modern commercial copper—is higher than the value chosen as standard in 1914, and, if the mass values are converted to volume conductivities by the use of conversion factors assuming the standard density of 8.89, the results will be low by as much as 0.74 per cent. This is important if comparison is to be made with other materials or with the results of other methods for the determination of conductivity. Except for copper conductors, conductivities are generally expressed in terms of dimensions rather than weight. In fact, the conductivity of the International Annealed Copper Standard is itself stated in terms of volume, and mass conductivities are used only because they are easier to determine. The authors' figure for the mass conductivity of annealed pure copper (102.3 per cent I.A.C.S., density of 8.956 grams per c.c.) is equivalent to a volume resistivity of 1.6730 microhm-cm. at 20°C., or a volume conductivity of 103.06 per cent I.A.C.S.

A. M. WIGHTMAN,† North East, Pa.—It is not proper to sharpshoot at so excellent a paper, but I notice that the density of a commercial wirebar, with no reduction, is given as 8.9314. Would that mean as cast? Is that not a rather high figure, and does it not conflict with such work as Corson's on the bulk density?

* Research Chemist, Raritan Copper Works.

† Staff Adviser, International Nickel Co.

‡ Professor of Metallurgy, Massachusetts Institute of Technology.

* Research Metallurgist, American Brass Co., Waterbury, Conn.

† The Electric Materials Co.

C. R. HAYWARD,* Cambridge, Mass.—I want to emphasize what has already been said by the chairman, that we are certainly on the right track in starting with very pure material. I have urged for many years that we pay more attention to minute quantities of impurities in copper, and I feel that now with a pure material to start with we may determine some of the real properties of this metal.

Mr. Skowronski was one of the pioneers in determining the effects of various impurities in copper, and I know he rejoices, as all of us do who are interested in copper, that perhaps some improvement can be made in the accuracy of the results which at the time he made them were outstanding.

In regard to Dr. Chipman's remarks, I wonder if his traces of carbon are not due to a very slight solubility of carbon monoxide, which obviously would be present. Contact with the crucible might also add some graphite, mechanically suspended.

J. S. SMART, JR. (authors' reply).—Mr. Baldwin's comments are welcome, as they represent an extension of the data along lines that the authors have not had occasion to pursue up to the present time. It is unfortunate, of course, that the limitations of the data necessitate such a lengthy extrapolation, and the authors are aware that additional points would have been desirable.

A comprehensive survey of the grain-size characteristics at low reductions has not been carried out, and we are not entitled to specifically answer Mr. Wise on the basis of our present data. However, we have observed that pure copper, reduced 10 to 20 per cent, exhibits a tendency to form a rather large recrystallized grain size, which is fairly stable, and prone to resist increase by grain growth. The initial grain size of the annealed strip used for the test deformations was rather high, and the results are not considered as conclusive.

Dr. Smith's distinction between mass and volume conductivities is a timely contribution, which deserves emphasis. The possibility of the occurrence of a significant change in the properties of the hard-drawn wire at room temperature during the interval between drawing and

annealing has been mathematically considered by Mr. Baldwin. Other general observations confirm the premise that detectable change did not occur. Following cold-drawing, a maximum of two hours elapsed before the annealing tests were begun. These were not run in any predetermined sequence, but entirely at random. The curves were progressively roughed out as the data accumulated, and filled in as necessary. Since the elapsed time between the beginning and end of the annealing treatments produced no detectable inconsistencies of the type under consideration in the curves, or in check samples run at different times, the authors feel that this source of error can safely be dismissed as negligible.

Mr. Wightman's question affords opportunity to emphasize the fact that all of the present density measurements on oxygen-bearing copper were performed on annealed wire, which had been rolled from a suitable cast shape to rod, cold-drawn 33 per cent, and annealed 1 hr. at 600°C. This annealed wire represents the 0 per cent reduction condition of Table 3. The density measurements made on castings are listed in columns 1 and 2 of Table 3, and these apply only to the continuously cast oxygen-free condition, with the indicated degree of cold-work.

Professor Hayward and Dr. Chipman have both discussed the presence of some form of carbon as an impurity in the pure copper rod, a possibility that is irrefutable, but difficult to approach by direct means. The indirect evidence afforded by conductivity tests after suitable heat-treatment, and by internal oxidation, was deemed sufficient to negate the possibility of significant interference by soluble carbon with the properties of the copper. Ransley has demonstrated that carbon monoxide will not diffuse through a thin copper diaphragm, thus effectively eliminating solubility in this form. The third and most likely possibility is that of mechanical inclusion, and this may well account for the failure of Dr. Chipman's analyses to depend on temperature. The authors have no evidence that could either prove or disprove this circumstance, which would apply to any material used as a crucible, but feel that the slow withdrawal of the solidified rod from the bottom of a quiet bath should minimize this effect to a considerable degree.

* Professor of Process Metallurgy, Massachusetts Institute of Technology.

Solubility of Sulphur Dioxide in Molten Copper

BY CARL F. FLOE* AND JOHN CHIPMAN,* MEMBERS A.I.M.E.

(New York Meeting, February 1941)

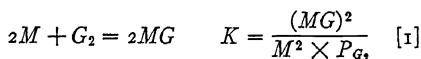
THE system molten copper-oxygen-sulphur is of interest from both the practical and theoretical standpoints; practically, because oxygen and sulphur play an important role in the commercial production of copper, and theoretically because it offers a chance to study the reaction between an oxide gas, SO_2 , and a molten metal. Reactions of this type, such as that between CO or CO_2 and molten iron, are important in many metallurgical operations. Again, the determination of any gas-metal equilibrium is of theoretical interest and value insofar as it contributes to the general development of the laws for solution of gases in metals. This problem is being given an increasing amount of attention in modern metallurgy.

This paper is the first of a series and presents the results of a determination of the solubility of sulphur dioxide in molten copper at temperatures from 1100° to 1500°C ., and pressures from about 20 mm. of mercury to somewhat above atmospheric.

REVIEW OF PREVIOUS WORK

The solubility of gases in most liquids has been found to obey Henry's law, which states that for a fixed temperature the amount of gas dissolved is directly proportional to the pressure. However this law does not hold for liquid metals. Instead, it appears that for many gases, particularly

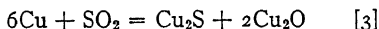
the simple diatomic ones such as O_2 , N_2 and H_2 , the amount dissolved in liquid metals is directly proportional to the square root of the pressure. This is known as Sieverts' law. It may be recognized as a special case of Henry's law, which applies when the solute gas is dissociated into atoms or when it reacts with the solvent metal to form solute molecules containing single atoms of the gaseous elements, as, for example:



which, if the solubility is not too high and the concentration of metal therefore nearly constant, can be simplified to:

$$MG = K_1 \sqrt{P_{G_2}} \quad [2]$$

Following the same reasoning, it would be expected that the solubility of SO_2 in copper would be proportional to the cube root of the pressure, the reaction being as follows:



$$K = \frac{\text{Cu}_2\text{S} \times (\text{Cu}_2\text{O})^2}{(\text{Cu})^6 (P_{\text{SO}_2})} \quad [4]$$

or, neglecting the change in metal concentration and considering that the concentrations of sulphur and oxygen are both proportional to the volume V of gas absorbed:

$$K_1 = \frac{V^3_{\text{SO}_2}}{P_{\text{SO}_2}} \quad \text{or} \quad V_{\text{SO}_2} = K_2 \sqrt[3]{P_{\text{SO}_2}} \quad [5]$$

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The only very extensive determination of the solubility of sulphur dioxide in copper was made by Sieverts and Krumbharr.¹ Contrary to expectation, the solubility was found to be more nearly proportional to the square root of the pressure than to the cube root, which could not be explained satisfactorily. Smithells² made a plot of the cube root of the pressure against the amount of gas dissolved in Sieverts' experiments and concluded that the experimental points lay very nearly on straight lines, which, however, did not pass through the origin.

Stubbs,³ on the basis of Sieverts' data, proposed that in this case the total solubility was a combination of molecular solution and chemical reaction, the former being proportional to the first power of the pressure and the latter to the cube root of the pressure as follows:

$$V_{\text{SO}_2} = k'P + k'' \sqrt[3]{P} \quad [6]$$

By calculation he found that at atmospheric pressure about 70 per cent of the total gas dissolved reacted chemically to form Cu_2S and Cu_2O while about 30 per cent was dissolved molecularly. At lower pressures the proportion chemically absorbed was considered to be greater, at higher pressures less. It is interesting to note that the method could not be successfully applied to the one experimental point available below 100 mm. pressure. Reference will be made to this later in connection with the present results.

The theory of molecular absorption does not seem reasonable in view of the great size of the SO_2 molecule. The more recent proposal by Lepp⁴ that solution of all gases in metals is a chemical process that can be explained on the basis of thermodynamics and chemical equilibrium seems to be more acceptable. However, Lepp explains that for the case of sulphur dioxide in copper the normal cube-root

relationship that would be expected from equations 4 and 5 does not hold because at the lower temperatures the dissociation of the sulphide phase is negligible and therefore the limit of solubility is determined by the dissociation of Cu_2O . The absorption then becomes proportional to the square root of the pressure. At higher temperatures the dissociation of Cu_2S becomes appreciable and the root of the pressure factor increases toward a maximum of 3. This reasoning is difficult to follow, as it would seem that such tendencies for dissociation are taken fully into account in the determination of the ordinary equilibrium constant for the reaction.

Sieverts and Bergner⁵ conducted further experiments on the solubility of sulphur dioxide in copper in which an excess of oxygen or sulphur was present. The results, however, did not make it possible to draw any further conclusions as to the nature of solution. An excellent review of the general subject of gases in molten copper has been made by Ellis.⁶ After reviewing the important work he concludes that "the solubility in copper of sulphur dioxide *per se* has yet to be determined."

In general it may be concluded that there is much disagreement as to the nature of the equilibrium between sulphur dioxide and molten copper. Since only one set of data, determined 30 years ago, is available, it was decided that a redetermination of the solubility limits would be of considerable value.

EXPERIMENTAL METHODS

The apparatus used for the determination of solubility, which in principle is similar to that first used by Sieverts, is shown schematically in Fig. 1. In making a run, 100 grams of copper was first melted in vacuum in the fused silica tube *A* using induction heating from the copper coil *B*. Induction heating was used principally because the stirring action on the molten

¹ References are at the end of the paper.

metal permitted equilibrium to be established more rapidly. Temperatures were read by a platinum-platinum rhodium thermocouple in a small silica tube *T*,

the first quantity of gas admitted had been reached, the stopcock *D* was again opened, another measured quantity of gas admitted, and the next equilibrium pressure deter-

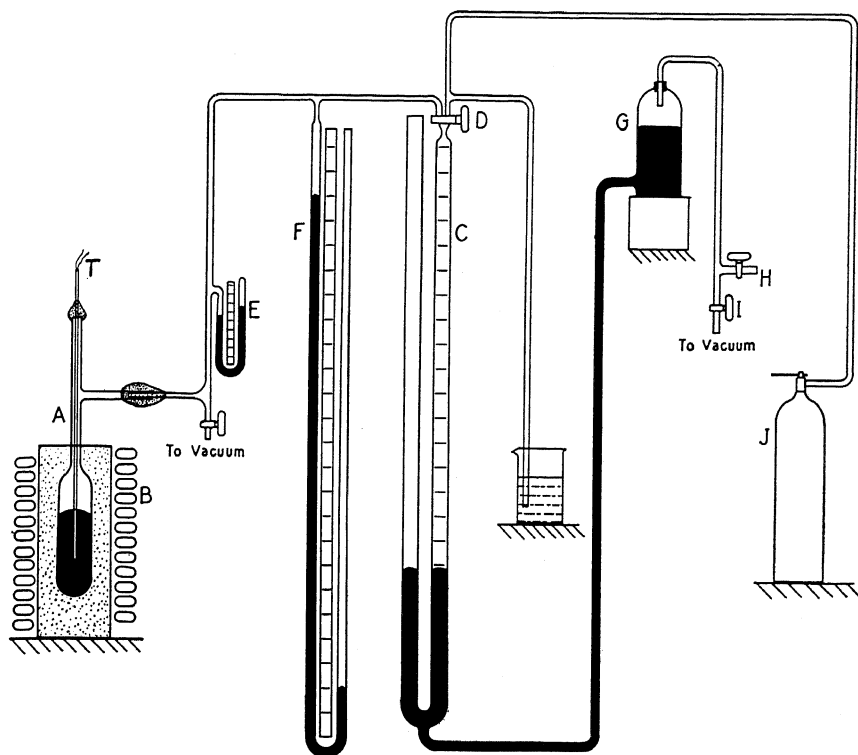


FIG. 1.—APPARATUS USED FOR DETERMINING SOLUBILITY OF SULPHUR DIOXIDE IN COPPER.

which was connected to an accurate potentiometer. The melting point of pure copper was used as a reference. Hand regulation of the power input permitted temperature control within $\pm 2^\circ\text{C}$.

After the copper was melted, the first equilibrium point was determined by admitting a measured amount of SO_2 gas from the burette *C* into the furnace side of the system through the stopcock *D*. Absorption of this gas by the molten copper continued until a constant pressure was reached. This usually took from 30 min. to 1 hr. The equilibrium pressure was read either by the closed-tube mercury manometer *E* or the open-tube mercury manometer *F*. After the equilibrium pressure for

mined. This was repeated until the pressure was somewhat above atmospheric.

In most runs two temperatures, 1100° and 1200°C . were used. In order to check the reversibility of the reaction, in some cases a point was first determined at 1100°C . then the temperature was increased to cause more absorption, and finally reduced again to 1100°C . in order that equilibrium might be reached by evolution of the gas. Above 100 mm. pressure the two results usually agreed within less than 0.5 per cent. However, below 100 mm. the difference was sometimes as much as 15 per cent. In general, results for different runs at low pressures were also inclined to be erratic. Pressures below 10

mm. could not be determined with very great accuracy.

Calculation of the composition of the molten copper in contact with the SO_2 gas at a given equilibrium pressure involves knowing how much of the total gas admitted to the furnace side of the system has been absorbed. This can be calculated if the so-called "hot volume" is known, or the volume of gas at standard conditions necessary to fill the furnace side of the system after the copper has been heated to the temperature at which the solubility is to be determined. This volume, of course, is less than the actual volume because of expansion of the gas in the vicinity of the molten copper. The determination of the hot volume was carried out with purified nitrogen, which is virtually insoluble in liquid copper.

The accuracy of solubility determinations made by this method is increased if the hot volume is kept as small as possible. In this work, owing to the design of the melting chamber and to the use of capillary tubing for all connections on the furnace side of the system, it was never greater than about 30 c.c.

For measuring gas into the furnace system a fixed mercury leveling bottle, *G*, was used, operating from the vacuum system. This permitted the mercury level in the burette to be controlled simply by the opening or closing of the stopcocks *H* and *I*. The sulphur dioxide from the cylinder *J* was dried by passing through phosphorus pentoxide before admission to the burette.

Commercial oxygen-free copper, O.F.-H.C. brand, in the form of $\frac{1}{8}$ -in. wire, was used for all experiments. This was kindly furnished by the Anaconda Copper Co. A check analysis after melting in vacuum in the furnace showed both the oxygen and the sulphur to be less than 0.001 per cent.

RESULTS OF EXPERIMENTAL WORK

The results for solubility determinations at temperatures ranging from 1100° to 1500°C. and varying pressures are given in

Table 1 and graphically in Figs. 2 and 3. The last column of Table 1 shows the calculated concentration of sulphur or oxygen in molten copper that is in equilibrium with the sulphur dioxide gas at the various pressures given.

TABLE 1.—*Solubility of Sulphur Dioxide in Molten Copper at Various Temperatures and Pressures*

| Run No. | Temperature, Deg. C. | Equilibrium Pressure, Mm. Hg | SO_2 Absorbed per 100 Grams Cu, C.c. | Sulphur or Oxygen, Per Cent |
|---------|----------------------|------------------------------|---|-----------------------------|
| 6 | 1100 | 13.9 | 8.3 | 0.0119 |
| | | 20.7 | 19.9 | 0.0284 |
| | | 30.9 | 29.2 | 0.0417 |
| | | 56.1 | 44.5 | 0.0636 |
| | | 129.0 | 77.6 | 0.111 |
| | | 642.0 | 146.4 | 0.209 |
| | | 893.0 | 165.5 | 0.236 |
| | 1200 | 19.6 | 19.1 | 0.0271 |
| | | 28.0 | 29.3 | 0.0419 |
| | | 43.9 | 44.9 | 0.0642 |
| | | 100.0 | 78.4 | 0.112 |
| | | 410.0 | 153.3 | 0.222 |
| | | 583.5 | 179.0 | 0.256 |
| | | 796.0 | 204.4 | 0.292 |
| 7 | 1100 | 11.6 | 20.6 | 0.0294 |
| | | 37.0 | 45.9 | 0.0656 |
| | | 89.5 | 69.4 | 0.0991 |
| | | 309.5 | 110.4 | 0.158 |
| | | 604.4 | 144.5 | 0.206 |
| | | 898.5 | 170.5 | 0.244 |
| | 1200 | 9.8 | 20.7 | 0.0296 |
| | | 25.1 | 46.2 | 0.0660 |
| | | 56.0 | 70.4 | 0.1005 |
| | | 187.0 | 114.8 | 0.164 |
| | | 371.0 | 153.6 | 0.220 |
| | | 590.0 | 184.5 | 0.264 |
| | | 804.0 | 208.5 | 0.298 |
| | 1300 | 752.0 | 251.0 | 0.358 |
| 8 | 1100 | 13.8 | 19.8 | 0.0283 |
| | | 50.0 | 50.1 | 0.0716 |
| | | 145.0 | 80.0 | 0.114 |
| | | 376.0 | 116.4 | 0.166 |
| | | 654.0 | 146.9 | 0.210 |
| | | 914.0 | 167.8 | 0.240 |
| | 1200 | 12.0 | 19.8 | 0.0283 |
| | | 34.0 | 50.6 | 0.0723 |
| | | 90.0 | 81.7 | 0.117 |
| | | 231.0 | 121.7 | 0.174 |
| | | 420.0 | 156.8 | 0.224 |
| | | 614.0 | 182.3 | 0.260 |
| | | 830.0 | 203.6 | 0.290 |
| | 1300 | 711.0 | 242. | 0.346 |
| 9 | 1200 | 771.0 | 197. | 0.281 |
| 11 | 1400 | 755.0 | 300. | 0.428 |
| | 1500 | 755.0 | 352. | 0.501 |
| | 1200 | 760.0 | 211. | 0.301 |
| 12 | 1500 | 764.0 | 365. | 0.522 |

Fig. 2 graphically illustrates how the volume of sulphur dioxide absorbed per 100 grams of copper changes with pressure at

1100° and 1200°C. The points obtained for the different runs, No. 6, No. 7, and No. 8, are shown by different symbols. These points show that each set lies on a fairly

reaction between the fused silica tube and the melt, the amount of this reaction varying with the time and temperature. Another reason is possible slight differences in the

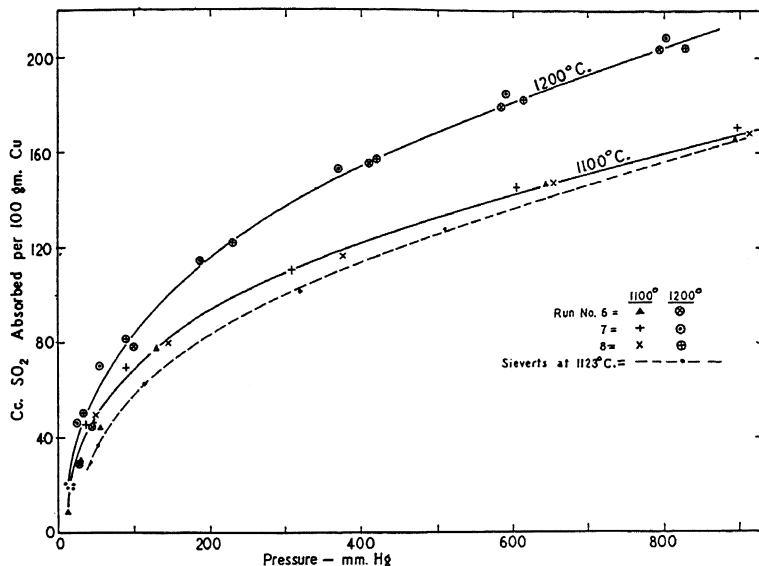


FIG. 2.—SOLUBILITY OF SULPHUR DIOXIDE IN COPPER AS A FUNCTION OF PRESSURE.

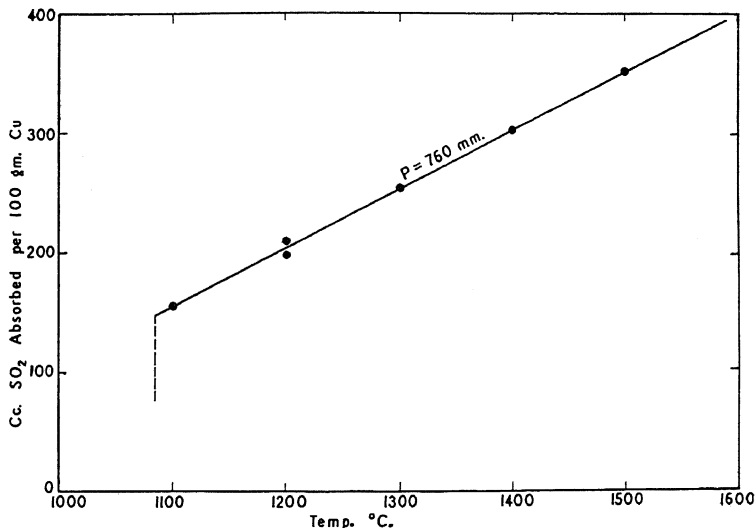


FIG. 3.—SOLUBILITY OF SULPHUR DIOXIDE IN COPPER AT ONE ATMOSPHERE PRESSURE AS A FUNCTION OF TEMPERATURE.

smooth curve, but that the results for different runs do not duplicate one another exactly, although they are reasonably close at the higher pressures. One reason for lack of duplication is that there is a slight

composition of the original copper, although this effect is not believed to be large. Runs No. 8, No. 9, No. 11, and No. 12 were deoxidized with hydrogen and then evacuated before any sulphur dioxide gas was admitted

to the furnace system, while runs No. 6 and No. 7 were not hydrogen-treated.

Fig. 2 shows also the results obtained by Sieverts for a temperature of 1123°C. In general, the solubilities found are somewhat

where V_{SO_2} is the number of cubic centimeters of sulphur dioxide at one atmosphere dissolved per 100 grams of copper, and t is the temperature in degrees centigrade.

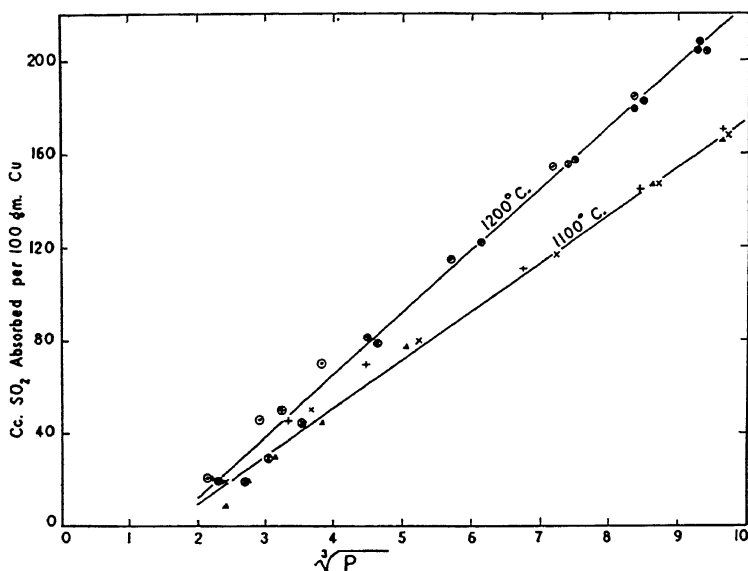


FIG. 4.—SOLUBILITY OF SULPHUR DIOXIDE IN COPPER AS A FUNCTION OF THE CUBE ROOT OF THE PRESSURE.

See Fig. 2 for an explanation of the symbols.

higher than those obtained by Sieverts, although the general shape of the curve is the same. The tendency for somewhat erratic results at low pressures was not noted by Sieverts because very few points were determined in this region. Fig. 2 shows also that at pressures below 20 mm. the temperature coefficient of solubility was very small. With increasing pressure, this coefficient increased rapidly.

Fig. 3 shows the way in which the solubility of sulphur dioxide in molten copper at one atmosphere pressure varies with temperature from the melting point to 1500°C. This solubility is directly proportional to the temperature. The equation for the curve within the limits of error of the experiments may be expressed by:

$$V_{SO_2} = -400 + 0.50t \quad [7]$$

There was considerable evolution of sulphur dioxide gas as the copper solidified. The amount of this could not be measured accurately because of cracking of the silica

TABLE 2.—Analysis of Ingots for Sulphur and Oxygen

| Run No. | S, Per Cent | O, Per Cent | Cubic Centimeters Remaining from S Analysis | Cubic Centimeters Remaining from O Analysis |
|---------|-------------|-------------|---|---|
| 6 | 0.081 | | 57 | |
| 7 | 0.071 | | 50 | |
| 8 | 0.047 | 0.073 | 33 | 51 |
| 9 | 0.039 | 0.044 | 27 | 31 |
| 11 | 0.032 | 0.050 | 22 | 35 |

tube as solidification took place. The best estimate that could be made indicated that the amount remaining in the solid ingot was of the order of 50 c.c. per 100 grams of

copper. This is present as cuprous oxide, cuprous sulphide, and occluded gas in the blowholes formed during freezing. All of the ingots from these melts showed high porosity.

coordinate and the volume of gas dissolved as the other. This is shown in Fig. 4. The points are represented reasonably well by a straight line at both 1100° and 1200°C., but the extension of these lines would in

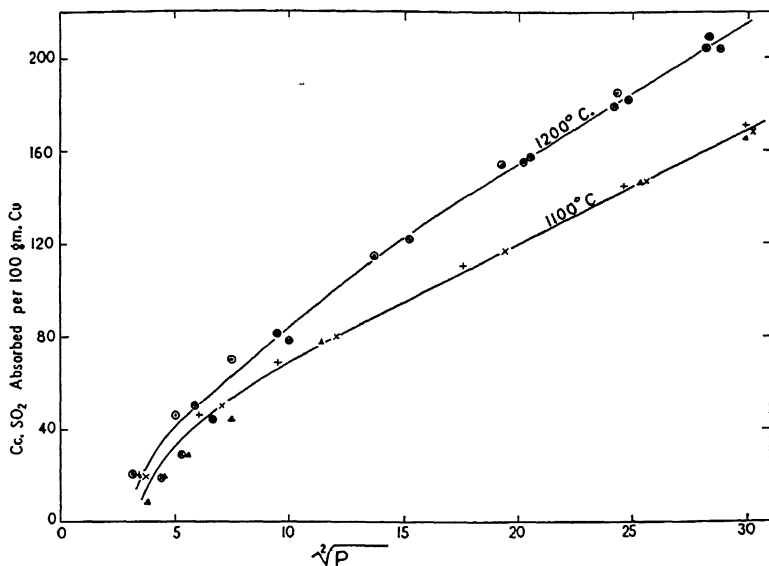


FIG. 5.—SOLUBILITY OF SULPHUR DIOXIDE IN COPPER AS A FUNCTION OF THE SQUARE ROOT OF THE PRESSURE.

See Fig. 2 for an explanation of the symbols.

The chemically combined sulphur and oxygen present in the ingots after solidification was determined by analysis, with the results shown in Table 2.

The oxygen was determined by the vacuum-fusion method, the accuracy of which for materials of this type is questionable. The results for sulphur show that the amount retained after solidification varies considerably, being equivalent to from 22 to 57 c.c. of sulphur dioxide.

DISCUSSION OF RESULTS

When Sieverts' law is extended to triatomic gases such as SO_2 , it would be expected that the volume of gas dissolved would be approximately proportional to the cube root of the pressure. The results given in Table 1 therefore have been plotted using the cube root of pressure as one

both cases intersect the pressure axis at a value of about 1.6 rather than at the origin. Smithells² has shown that Sieverts' results give a similar curve.

The solubility above 20 mm. may be expressed by an equation of the form:

$$V_{\text{SO}_2} = K(\sqrt[3]{P} - 1.6) \quad [8]$$

for 1100°C., $K = 21.0$, while for 1200°C., $K = 27.0$. However, it is believed that this equation is only of empirical significance, since there is no obvious explanation for it in terms of any reasonable hypothesis regarding the nature of the solution.

Sieverts suggested that his results more nearly showed the solubility to be proportional to the square root of the pressure. To check this, the values given in Table 1 were plotted in this way, as shown in Fig. 5. This was not as successful as plotting

the cube root of the pressure. The extension of the nearly straight-line portion of the curves intersects the vertical axis above the origin, while the values for low pres-

expected from the log plot; namely, that at pressures above about 100 mm. a straight line is obtained, the extension of which would pass through the origin. However,

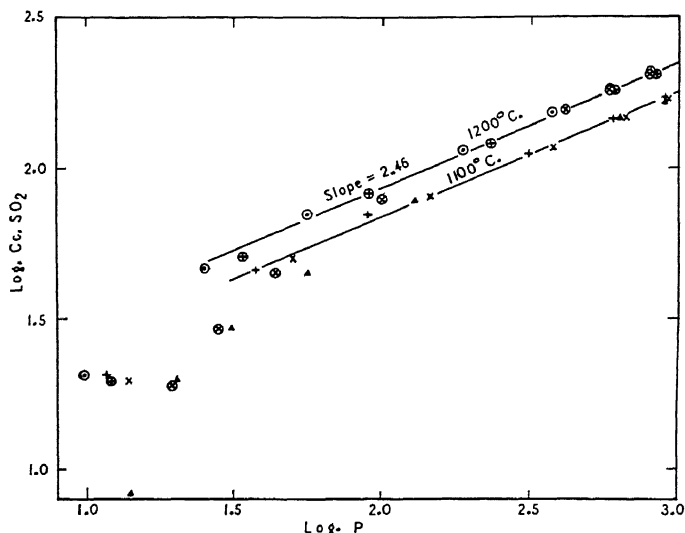


FIG. 6.—LOGARITHMIC PLOT OF NUMBER OF CUBIC CENTIMETERS OF SULPHUR DIOXIDE DISSOLVED PER 100 GRAMS OF COPPER VERSUS LOGARITHM OF PRESSURE.

See Fig. 2 for an explanation of the symbols.

sures fall off rapidly and, if extended, would intersect the pressure axis at about 3. There is, of course, no fundamental reason why the amount of sulphur dioxide absorbed by molten copper should be proportional to the square root of the pressure.

Next, in order to try to interpret the results, a plot of the logarithm of the amount of SO_2 absorbed versus the logarithm of the pressure was made for runs No. 6, No. 7, and No. 8 at 1100° and 1200°C . (Fig. 6). All of these curves approach almost the same constant value of slope at high pressures, the average being 2.46. However, as the pressure is decreased, the slope rapidly decreases, indicating that it is not possible to make the absorption proportional to any single root of the pressure over the entire range.

In order to show the effect of raising the pressure to the $1/2.5$ power, a graph was made (Fig. 7). The result is what would be

at low pressures the values again fall away toward the pressure axis.

These results are interpreted as indicating that no simple reaction between the gas and the metal can account for the data. The failure of the initially postulated reaction (Eq. 3) is demonstrated graphically in Fig. 8, where the ratio

$$\frac{(\% \text{ S})(\% \text{ O})^2}{P_{\text{SO}_2}} \quad [9]$$

is plotted against the pressure. It is evident that the "equilibrium constant" is never strictly constant and actually appears to approach zero at low pressures! In these calculations, the concentration of copper has been assumed to be constant. If the proper values for copper concentration were used, it would shift the results only slightly, but in such a way as to increase the variability of the ratio.

Stubbs³ attempted to explain these discrepancies by assuming that a part of the sulphur dioxide was dissolved molecularly as shown by Eq. 6. This can be done fairly

for run No. 8 at 1200°C. The results are shown in Table 3. The amount of assumed chemical solubility was 50 per cent, 70 per cent and 90 per cent, respectively, of the

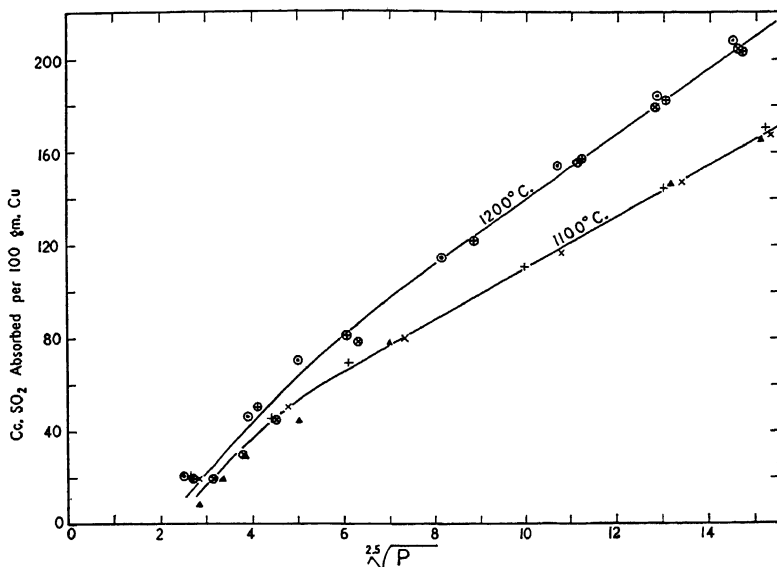


FIG. 7.—SOLUBILITY OF SULPHUR DIOXIDE IN COPPER AS A FUNCTION OF THE $1/2.5$ POWER OF PRESSURE.

For an explanation of the symbols, see Fig. 2.

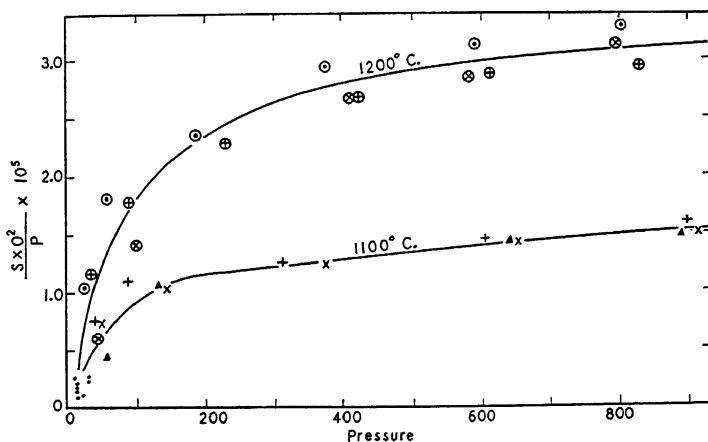


FIG. 8.—“EQUILIBRIUM CONSTANT” FOR REACTION BETWEEN SULPHUR DIOXIDE AND COPPER (EQUATION 3) AS A FUNCTION OF PRESSURE.

See Fig. 2 for an explanation of the symbols.

successfully for pressures above 100 mm., but becomes unreasonable when the pressure is below 100 mm. To illustrate this, values of K'' from Eq. 6 were calculated

total sulphur dioxide dissolved at the highest pressure. These results show that for pressures below 100 mm. the constant is far too small, which agrees with the

TABLE 3.—Values of K'' of Equation 6 Calculated from Assumed Partial Molecular Solution

RUN No. 8, 1200°C.

| Per cent SO ₂ chemically dissolved at 830 mm..... | 50 Per Cent | 70 Per Cent | 90 Per Cent |
|--|-------------------|-------------------|-------------------|
| Corresponding values for K' .. | 0.1226 | 0.0736 | 0.0246 |
| Values for K'' at P | | | |
| 12 mm..... | 8.0 | 8.3 | 8.5 |
| 34 mm..... | 14.3 | 14.8 | 15.4 |
| 90 mm..... | 15.8 | 16.8 | 17.7 |
| 231 mm..... | 15.2 | 17.1 | 18.9 |
| 420 mm..... | 14.1 | 16.8 | 19.6 |
| 614 mm..... | 12.6 | 16.1 | 19.7 |
| 830 mm..... | 10.8 | 15.2 | 19.5 |

data plotted in Fig. 8. No assumption of partial molecular solubility can correct this discrepancy.

In all of these calculations for equilibrium constants it was assumed that the activity of the sulphide and oxide dissolved in the copper was proportional to the concentration. This would be true for perfect solutions, but may not be true over the range of compositions covered. The conventional interpretation would be that activity is proportional to concentration in dilute solutions, but that the ratio of activity to concentration decreases with increasing concentration. For the data given in Table 3, this would imply that the more concentrated solutions deviate widely from ideal behavior, a conclusion that is contradicted by the observed normal lowering of the melting point of copper both by the oxide and by the sulphide.⁷

These considerations lead to the tentative conclusion that the anomalous results are due to irregular behavior of the dilute solutions rather than to deviations from ideality at the higher concentrations.

In attempting to explain the low solubility at low pressures, it was first thought possible that the sulphur dioxide was broken down to sulphur monoxide by solution of one atom of the oxygen. This would have the effect of causing the pres-

sure to remain constant or at a higher than normal value. However, calculations based on the data for the free energies of sulphur monoxide and sulphur dioxide given by Montgomery and Kassel⁸ and Cross⁹ show that this effect would be negligibly small.

SUMMARY AND CONCLUSIONS

The solubility of sulphur dioxide in molten copper has been determined over the range of pressure from about 20 mm. Hg to 900 mm. Hg, and temperatures from 1100° to 1500°C. The data show that the solubility cannot be interpreted by postulating any simple chemical reaction between the gas and the metal. The equation for solution that would normally be written (Eq. 3) does not hold, particularly at low pressures. The indications are that this is due to some irregular behavior of the dilute solutions, which cannot be readily explained on the basis of our present knowledge of the nature of solution of gases in molten metals.

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DISCUSSION

(S. Skowronski presiding)

O. W. ELLIS,* Toronto, Ont.—There is an interesting point in connection with the method of melting the copper described by the authors. The question arises whether the temperature of the gas immediately above the metal and somewhat distant from the metal is at the same temperature as the metal itself.

Some years ago the writer propounded the following question to Prof. N. Rashevsky:

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Suppose a hot body maintained at a temperature $T^\circ\text{K}$ is put into an atmosphere of any gas having a pressure P_0 and a temperature T_0 . When a stationary state is reached, the temperature of the gas in the immediate neighborhood of the body will be T , while at a point far enough remote it will be T_0 . The variation of temperature from point to point will depend on the shape and size of the body, as well as on the heat conductivity of the gas. At first glance it might appear that the pressure within the gas would be the same at all points, since the gas is supposed to be at rest and no convection currents are assumed. However, more detailed consideration shows that this is not true. The question arises whether the pressure of the gas will be the same at the surface of the body as at some distance from it; that is, whether it will be equal at all points to P_0 or not. Professor Rashevsky's solution of the problem follows:

"A rigorous solution of the problem is, however, very difficult since we have here to deal with a nonequilibrium state and the relations of the kinetic theory, which are all obtained on the assumption of a thermal equilibrium—that is, of a temperature constant throughout the whole gas—do not apply here. The problem is intimately connected with the theory of radiometric forces, and up to the present no entirely satisfactory solution of these problems has been given. The earlier works of M. Knudsen dealt principally with gases at low pressures. Without this restriction the problem has been investigated by Westphal, but the solution was later on recognized as incorrect by the author himself. A paper by E. Einstein [*Ann. Phys.* (1922) 69, 241] treats the problem in a very general way, but the final formulas are of no use for the case which interests us here. A simplified treatment of the problem has been given more recently by E. Einstein [*Ztsch. Phys.* (1924) 27, 1] in which all assumptions are schematical, and only the order of magnitude of the results, not an exact theory, is claimed.

"Following here the same simplified assumptions as in A. Einstein's paper, we will generalize them so as to obtain an answer to the question that interests us.

"We first of all suppose that the hot body is limited by a plane, which we choose as the yz plane of our system of coordinates. Then there

is a drop of temperature along the x axis, which drop is supposed to be given at every point. If we neglect, as does Einstein, the velocity distribution of molecules and assume that they all have the same velocity u which is connected with the temperature T of the gas by the relation

$$\frac{1}{2}mu^2 = \frac{3}{2}KT \quad [1]$$

where m is the mass of the molecule, and K is Boltzmann's constant, then through a unit area perpendicular to the x axis $\frac{1}{6}nu$ molecules will pass per second, where n is the number of molecules in a cubic centimeter. But since there is no transport of gas, the number of molecules passing the area considered in the positive direction of x must be equal to the number of molecules passing in the negative direction. Also, there should be no accumulation of gas in certain regions. Hence nu must be constant, which together with Eq. 1 shows that n is inversely proportional to \sqrt{T} . More exactly this is seen from the following:

"Consider a general case when there is a transport of mass of gas due to inequality of temperatures, as well as to inequality of concentrations. The case of inequality of concentration alone, at uniform temperature, would lead to the usual phenomenon of diffusion. In the more general case we proceed in a way similar to that for diffusion. Consider two planes parallel to yz ; namely, x and $x + \Delta x$. The number of molecules contained in a parallelepiped formed by two unit areas on x and $x + \Delta x$ is $n\Delta x$. The variation of this number per second is equal to the difference of the number of molecules entering through the plane x , and that leaving the plane $x + \Delta x$. The first is

$$\frac{1}{6}n_x u_x \quad [2]$$

where the index x shows that the corresponding quantities are taken at the point x . The second is equal to

$$\frac{1}{6} \left(n_x + \Delta x \right) u_x + \Delta x = \frac{1}{6} \left(n_x u_x + n_x \frac{\partial u_x \Delta x}{\partial x} + u_x \frac{\partial n_x \Delta x}{\partial x} \right) \quad [3]$$

neglecting quantities of higher order.

"Hence the difference equals

$$\frac{1}{6} \left(n_x \frac{\partial u_x}{\partial x} + u_x \frac{\partial n_x}{\partial x} \right) \Delta x$$

and this should be equal to

$$\frac{\partial n}{\partial t} \Delta x$$

Hence

$$\frac{1}{6} \left(n \frac{\partial u}{\partial x} + u \frac{\partial n}{\partial x} \right) = \frac{\partial n}{\partial t}$$

For a stationary state, such as we consider

$$\begin{aligned} \frac{\partial n}{\partial t} &= 0, \text{ and Eq. 3 reduces to} \\ n \frac{\partial u}{\partial x} + u \frac{\partial n}{\partial x} &= \frac{\partial(nu)}{\partial x} = 0 \end{aligned} \quad [4]$$

Hence

$$nu = \text{constant, or using Eq. 1}$$

$$n \sqrt{\frac{3KT}{m}} = \text{constant} \quad [5]$$

and

$$n = \frac{A}{\sqrt{T}} \left(A = \frac{\text{const.}}{\sqrt{\frac{3K}{m}}} \right) \quad [6]$$

"If the body is at a temperature of 1200°K., while the surrounding gas (say air) is at 300°K., the concentration in the immediate neighborhood of the boundary of the body will be two times smaller than at a remote point. But with the approximations used here, there is also for a nonuniform temperature in the gas

$$P = nKT \quad [7]$$

Combining this with Eq. 6 gives

$$P = B \sqrt{T} \quad (B = AK) \quad [8]$$

"Hence, the pressure increases as the square root of temperature. In the case just mentioned, the pressure will be twice as large at the boundary as at a remote point.

"With the degree of approximation used here, we may apply these formulas also to partial pressures and concentrations, say of H₂O vapors in air.

"It should be remarked that although both pressure and concentration in the neighborhood of the hot body differ from those at a remote point, the number of molecules striking a unit surface of the body per second is the same as though the body were cold. In applying these considerations to the calculations of solubility of water vapor in a melted metal exposed to air, by applying Henry's law, one has therefore to consider the question as to what is character-

istic for the solubility of a gas, the pressure, or the quantity of molecules striking the surface of the metal per second.

"As mentioned above, the considerations here give only an estimation of the order of magnitude of the quantities involved."

It will be observed that Professor Rashevsky refers in particular to "calculations of solubility of water vapor in a melted metal exposed to air." This was the particular gas with which the writer was concerned at the time of his inquiry. The writer feels, however, that whether water vapor or sulphur dioxide is in question, some consideration should be given to Professor Rashevsky's answer, in view of its quite general application.

In other words, the writer feels it desirable to ensure, if possible, that the temperature of the gas above the molten metal be held throughout at the same temperature as the molten metal itself. This, of course, would involve a change in the design of the furnace used in solubility experiments.

S. SKOWRONSKI,* Perth Amboy, N. J.—Formerly when discussing the solubility of sulphur dioxide in copper we had to refer to Sieberts' work, but technically this work is ancient and we are indebted to the authors of this paper for furnishing us with more up-to-date data, more in line with the present theories of gases in metals.

Commercially there is another phase of the problem that should be investigated; that is, the effect of sulphur dioxide in copper in the presence of hydrogen, with a diminishing amount of oxygen in the copper. There is no question in my mind that at some stage hydrogen sulphide must be formed, but this has never been proved, and if it could be proved it would go a long way toward explaining the overpoling phenomenon and the peculiar behavior of gassy copper.

As far back as 1918, Carpenter and Elam, in their classical work on the gases in Admiralty bronze (88-10-2), found that the predominating gas was hydrogen sulphide; they also found indications of this gas in one brand of refined copper, and reported hydrogen sulphide or sulphur dioxide as the predominating gas in this brand of copper. Research work is needed

* Research Chemist, Raritan Copper Works.

to differentiate between the action of hydrogen sulphide and sulphur dioxide in refined copper.

C. R. HAYWARD,* Cambridge, Mass.—In some work done by myself and two co-workers,¹⁰ perhaps the most astonishing thing found was the behavior of sulphur dioxide as it came in contact with copper flowing from a crucible to a mold.

The other gases—hydrogen, nitrogen and various others—were very mild in their effect, but sulphur dioxide would attack the copper with great avidity. A crucible containing about 30 lb. of molten copper at 1150° was opened with a plug at the bottom, and the copper flowed into a mold into which a small stream of liquid sulphur dioxide was flowing. The copper absorbed the gas and swelled to nearly twice its volume, and the odor of sulphur dioxide on the copper after it was taken out was noticeable. This copper definitely showed considerable oxygen, although copper melted in the same way poured into nitrogen showed no sign of oxygen.

We do not know how complete the reaction was and to what extent sulphur dioxide was dissolved in the copper, but there was considerable indication that sulphur dioxide gas was taken up in that very short period of time and evolved subsequently, giving the very porous ingots that were obtained.

Of course, the commercial possibilities belong in the part of the curve that is most irregular, as far as the results obtained by the present authors are concerned.

When Mr. Skowronski suggests the possibility of the presence of hydrogen sulphide I do not believe that we can ignore him. I believe that there is a possibility that hydrogen sulphide may be one of the gases involved, and since the low pressures most interest the commercial copper refiner, I hope that someone will more carefully study this portion of the curve and in so doing consider the suggestions made by the chairman.

Also, in further work on this subject, I hope that some sulphur-free copper can be used as a basis of the experiments.

J. CHIPMAN.—I want especially to thank Mr. Skowronski for his suggestion regarding

the study of hydrogen sulphide in liquid copper. One of our major objects in presenting this work at this stage was that we hoped to get just such suggestions, which will be valuable to us, I am sure, in future work along this line.

The very strong avidity of liquid copper for sulphur dioxide, which Professor Hayward mentioned, is of course obvious in the solubility data when you think of a hundred grams of copper, which has a volume of about 12 c.c., and which can dissolve an amount of gas that would occupy 200 to 300 c.c. at standard conditions and actually occupies perhaps 1000 to 1500 c.c. at the temperature of liquid copper. That is a reaction that obviously has considerable avidity. It is one of the highest gas-solubility phenomena that we know of.

C. F. FLOE AND J. CHIPMAN (authors' reply).—The question of the effect of using induction heating, raised by Dr. Ellis, was considered. It was concluded that some temperature difference between the gas above the metal and the metal itself would exist, but that this would not affect the solubility. Since Dr. Ellis' comments were received, the question has again been considered. Several experts in kinetic theory have been consulted, particularly Dr. Walter H. Stockmayer, of the Department of Chemistry, Massachusetts Institute of Technology. The conclusion is that the calculations quoted by Dr. Ellis do not apply to the apparatus used in these experiments. Kinetic theory and experiment concur in the prediction that as long as the mean free path of the molecules is small compared to the diameter of the tube no pressure differences can persist, even though the temperature be different in different sections of the tube. The equality of pressure is maintained through mass flow of the gas (convection). Rashevsky postulates, incorrectly, the absence of convection.

The phenomena discussed by Rashevsky are, however, predicted by kinetic theory for the case in which the tube diameter is much smaller than the mean free path. For such cases the constancy of p/\sqrt{T} is predicted, and was experimentally verified as far back as 1879.¹¹ A brief discussion of this phenomenon, known as thermal transpiration, is given by Kennard.¹²

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¹⁰ C. R. Hayward: Effect of Atmosphere during Casting of Copper. *Int. Inst. of Metals*.

¹¹ Reynolds: *Phil. Trans.* (1879) 170 (II), 727.

¹² Kennard: *The Kinetic Theory of Gases*, 66-67. New York, 1938. McGraw Hill Book Co.

The calculations of A. Einstein and E. Einstein quoted apply only to the case where the pressures are low and the vessel dimensions are small compared with the mean free path of the molecules. In the present case it can readily be shown that the mean free path is small compared with the tube diameter. To calculate this, use may be made of the formula:

$$L = \frac{kT}{\sqrt{2}\pi p\sigma^2}$$

where σ is the molecular diameter of SO_2 , found to be approximately 3.4 Å. from viscosity data. Taking the worst case of lowest pressure (10 mm.) and highest temperature (1800°K.) it is found that $L \approx 0.0036$ cm., which is small compared with the tube diameter used in the experiments. The conclusion is, therefore, that the pressures read on the manometer are equal to the pressures of SO_2 above the liquid copper.

Dr. Ellis, on the basis that some thermal transpiration takes place, concludes that the actual pressure at the liquid gas interface would be greater than at a remote point. This is interpreted as meaning that the actual pressure at the boundary between the liquid metal and the gas would be greater than the

pressure measured on the barometer. Such a condition, if anything, should have the effect of increasing the gas solubility, whereas the data actually show that, at low pressures particularly, the solubility is less than is predicted by Sieverts' law.

Professor Hayward comments that from the commercial point of view one is most interested in the irregular part of the curve. This is true and experiments to determine the very low-pressure solubilities are under way.

The authors believe that many of the discrepancies in the low-pressure region are due to small amounts of impurities in the metal. Experiments now under way show that an excess of either oxygen or sulphur in the metal greatly reduces the solubility of sulphur dioxide. Probably the maximum in solubility will occur when the initial copper is of highest purity. It is the authors' feeling that discrepancies from one run to the next, and also discrepancies in the low-pressure region, are principally due to the presence of small amounts of impurities in the original material.

Plans for further work include studies on the effect of impurities and the development of apparatus that will give more precise results at low pressures.

Solubility of Oxygen in High-purity Copper

By ARTHUR PHILLIPS,* MEMBER, AND E. N. SKINNER, JR.,† JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1941)

DURING the course of an experimental program concerned with the hydrogen embrittlement of copper containing oxygen in concentrations within the solubility limits it became necessary to make a critical appraisal of the literature dealing with the solubility relationships of oxygen and solid copper. The latest determinations, and perhaps the only data obtained on "spectroscopically" pure copper, are those of Rhines and Mathewson¹ who reported that the solid solubility increases from 0.007 per cent oxygen at 600°C. to about 0.015 per cent at 1050°C. Hanson, Marryat and Ford² had previously placed the solubility limit at less than 0.009 per cent oxygen at 1000°C. and Allen and Street³ had suggested, on the basis of an unpublished research by T. Hewitt, not over 0.005 per cent oxygen at 500°C.

In the introductory stages of the investigation indirect evidence accumulated to suggest that the solubility limits were significantly lower than those previously reported. For this reason it was deemed essential to clarify this point before proceeding with a program intended to establish a quantitative relationship between hydrogen embrittlement and oxygen concentrations positively known to be within the solid solution range. Furthermore, the increasing production and the highly selective applications of the commercial

"oxygen-free" coppers inevitably direct attention to the practical necessity for exact knowledge regarding the effects of minute concentrations of the elements ordinarily found in the high-purity coppers now available. Of these elements oxygen occupies a unique position, not only by virtue of its specific effects on copper but more particularly in view of its important reactive tendencies toward the other impurities with which it is associated.

Rhines and Mathewson considered several methods for measuring the solubility of oxygen and finally adopted the simple plan of saturating the specimens, obtained from redeposited cathode copper, by heating at the desired temperature in air. After the removal of surface oxide by mechanical and chemical means, the oxygen content was determined in the underlying metal. In general, this process of saturation, with a few modifications, was followed by the present writers. Although the procedure is direct and has obvious advantages, its effectiveness, unfortunately, is reduced by an excessive scaling of the copper, particularly at the higher temperatures. After saturation treatments above 900°C. the writers found that the specimens, necessarily rather thin in the original condition, consisted largely of scale and yielded too little metal for a satisfactory analytical sample. Furthermore, great difficulty was experienced in effecting complete removal of the scale. Needless to say, it is necessary to exercise extraordinary care in the preparation of the surface of the analytical sample in order to eliminate submicroscopic fragments of cuprous oxide which ordinarily are lodged in the crevasses and

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¹ References are at the end of the paper.

surface irregularities of copper oxidized at high temperatures. Scaling of a serious nature was encountered by Rhines and Mathewson and they stated that a troublesome source of error was introduced by the surface conditions of their saturated material.

EXPERIMENTAL PROCEDURE

In order to reduce the loss of metal by oxidation during the high-temperature treatments, the time of heating in air was short, simply that necessary to form a thin coat of oxide. After surface oxidation was effected the air was displaced by purified nitrogen, which served as a protective atmosphere during the remainder of the saturation period. By this procedure satisfactory specimens were obtained and the loss of copper, including the loss incurred by the mechanical and chemical cleaning of the surface, did not exceed 10 per cent. Later experiments, in which copper was saturated at temperatures ranging from 550° to 900°C. in air, stagnate and circulating nitrogen furnished excellent analytical checks. The oxygen content, determined by the indirect method of Bassett and Bedworth,⁴ was considered to be the percentage loss-in-weight of the sample after prolonged heating in pure hydrogen. Sulphur was, of course, determined simultaneously and the necessary correction applied to the total weight loss. For the supply of hydrogen for the combustion train, purified tank hydrogen* was substituted for the conventional Kip generator, in order to eliminate the presence of acetylene apparently formed from carbon in mossy zinc. Otherwise the analytical procedure was essentially that followed by Rhines and Mathewson.

* The gas was passed successively through hot copper chips, concentrated H_2SO_4 saturated with $\text{K}_2\text{Cr}_2\text{O}_7$, 10 per cent KOH saturated with KMnO_4 , concentrated $\text{H}_2\text{S}_2\text{O}_8$, stick KOH and finally dried by passing through granular CaCl_2 and glass wool containing P_2O_5 .

The copper used in the preliminary work was supplied by the United States Metals Refining Co. and consisted of O.F.H.C. copper of normal purity. From a 50-lb. slab, bars 1 in. thick were obtained by planing off the upper and lower portions of the cake. These bars were cold-rolled* to 0.10 in., a reduction of 90 per cent, with no intermediate anneals. Pieces cut from the strips were then saturated with oxygen, as previously described, at a series of temperatures ranging from 500° to 1040°C. The surface scale was broken and largely removed by tapping with a light hammer. After the surface of the pieces had been cleaned with emery cloth, the metal was pickled in 1:1 nitric acid. The specimens were then plunged into a beaker of cold water which had been previously boiled to remove oxygen and carbon dioxide. After this rinse the copper was dried rapidly by rubbing vigorously with a nap-free absorbent paper. Every effort was made to avoid superficial oxidation, as the surface layer was to be included in the chips taken for chemical analysis. The procedure described was found preferable to rinsing in ether and alcohol and eliminated the possibility of contamination by a residue from the organic solutions.

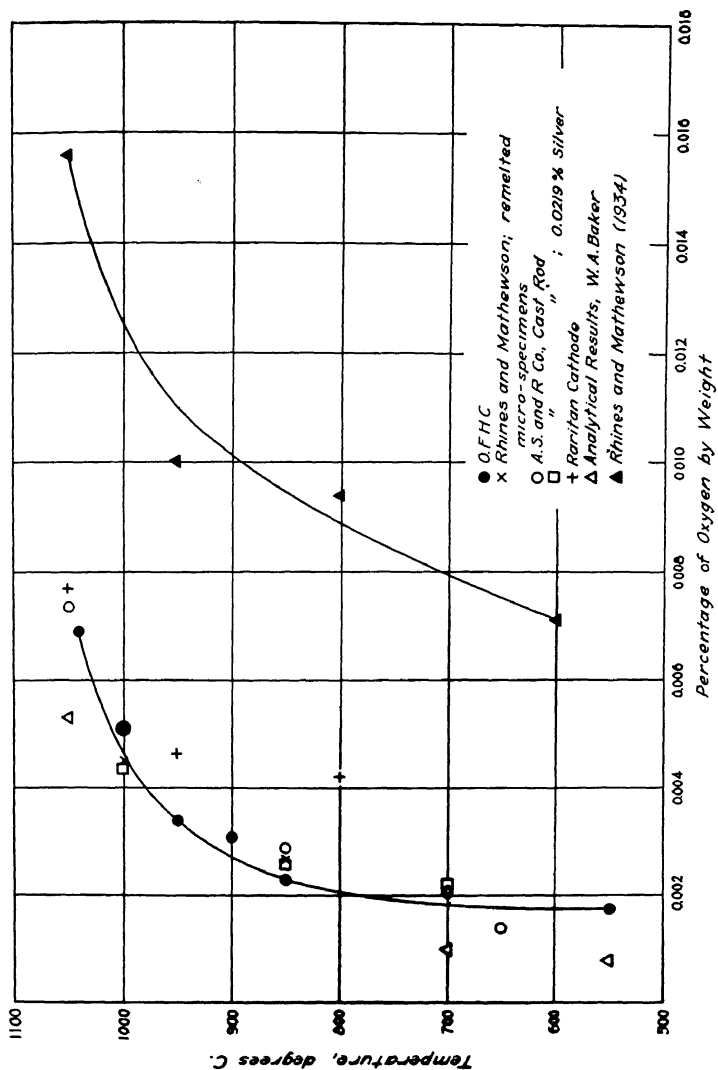
All samples for analysis were in the form of chips removed by a slowly operating shaper. After screening to remove the fines, the chips were weighed and introduced into the ignition bulb with the minimum of delay, in order to reduce the error due to surface oxidation. The heat-treatments involved, together with the oxygen and sulphur determinations, are summarized in Table 1 and the solubility curve plotted from the data is shown in Fig. 1, which also includes a reproduction of Rhines and Mathewson's curve. It is interesting to note that the sulphur content of the preoxidized specimens heated to 1000° and 1040°C. in

* The authors are indebted to the Bridgeport Brass Co. for the rolling of this material.

nitrogen was reduced from approximately 0.003 per cent to about 0.0004 per cent.

Since Rhines and Mathewson had used redeposited high-purity copper cathodes,

on chemical and spectrographic methods, which are hardly effective in yielding satisfactory analytical results on coppers containing impurities in minute concentra-



it was deemed imperative to extend the present investigations to coppers of various origins and impurity contents. Although this precaution is unquestionably desirable, an intelligent execution of the program was made difficult by the necessity of depending

tions. However, in spite of admittedly questionable quantitative expressions of impurity content, it is believed that the following results have been obtained on coppers differing sufficiently in this respect to afford oxygen-solubility data applicable

to the high-purity coppers of present day interest.

A prior treatment of Raritan cathode copper designed to eliminate sulphur and certain other impurities by high-tempera-

in Table 1 and the points are plotted in Fig. 1.

The writers were fortunate in securing from the American Smelting and Refining Co. a quantity of extremely high-purity

TABLE 1.—*Data on Solubility Limits of Oxygen in Copper*

| Kind of Copper | Temperature of Saturation, Deg. C. | Time of Saturation, Hr. | Atmosphere during Saturation | Oxygen, Per Cent by Weight | Sulphur, Per Cent by Weight |
|--|------------------------------------|-------------------------|------------------------------|----------------------------|-----------------------------|
| O.F.H.C. (as recd.) | 550 | 203 | Air | 0.0007 | 0.0027 |
| | 550 | 1600 | Air | 0.0018 | 0.0026 |
| | 700 | 75 | Air | 0.0017 | 0.0021 |
| | 700 | 90 | Air | 0.0020 | 0.0029 |
| | 850 | 35 | Air | 0.0021 | 0.0027 |
| | 850 | 50 | Air | 0.0022 | 0.0032 |
| | 850 | 65 | Air | 0.0023 | 0.0030 |
| | 850 | 65 | Air | 0.0025 | 0.0030 |
| | 900 | 21 | Nitrogen | 0.0027 | 0.0030 |
| | 900 | 30 | Nitrogen | 0.0035 | 0.0035 |
| O.F.H.C. | 900 | 33 | Nitrogen | 0.0030 | 0.0027 |
| | 950 | 40 | Nitrogen | 0.0034 | 0.0019 |
| | 1000 | 15 | Air | 0.0054 | 0.0033 |
| | 1000 | 20 | Air | 0.0050 | 0.0033 |
| | 1000 | 24 | Air | 0.0053 | 0.0031 |
| | 1000 | 20 | Nitrogen | 0.0055 | 0.0029 |
| | 1000 | 60 | Nitrogen | 0.0049 | 0.0004 |
| | 1000 | 65 | Nitrogen | 0.0046 | 0.0003 |
| | 1040 | 35 | Nitrogen | 0.0070 | 0.0004 |
| | 1040 | 35 | Nitrogen | 0.0068 | 0.0006 |
| Raritan cathode vacuum melted | 800 | 85 | Nitrogen | 0.0042 | 0.0002 |
| | 950 | 65 | Nitrogen | 0.0046 | 0.0002 |
| | 1050 | 30 | Nitrogen | 0.0077 | |
| A.S. and R. | 650 | 210 | Air | 0.0014 | |
| | 850 | 55 | Nitrogen | 0.0029 | |
| | 1000 | 25 | Nitrogen | 0.0045 | |
| | 1000 | 25 | Nitrogen | 0.0053 | |
| | 1000 | 25 | Nitrogen | 0.0055 | |
| | 1050 | 30 | Nitrogen | 0.0075 | |
| A.S. and R. containing 0.0219 per cent silver. | 1050 | 30 | Nitrogen | 0.0072 | |
| | 700 | 168 | Air | 0.0022 | |
| | 850 | 55 | Nitrogen | 0.0026 | |
| | 1000 | 30 | Nitrogen | 0.0043 | |
| Rhines and Mathewson remelted micro-specimens. | 1000 | 30 | Nitrogen | 0.0044 | |
| | 700 | 145 | Air | 0.0021 | |
| | 700 | 145 | Air | 0.0021 | |
| | 850 | 55 | Nitrogen | 0.0028 | |
| | 1000 | 50 | Nitrogen | 0.0044 | |
| | 1000 | 50 | Nitrogen | 0.0045 | |

ture vacuum melting in association with pure graphite furnished a supply of copper containing not over 0.0002 per cent sulphur and 0.0008 per cent oxygen. Incidentally, it is believed that the material used by Rhines and Mathewson for further refining came from this lot of copper. From the ingot so obtained, a strip 0.10 in. thick was prepared and pieces from it were saturated at 800°, 950° and 1050°C. The heat-treating schedule and the resulting oxygen determinations are also assembled

copper in the form of $\frac{3}{8}$ -in. rod. Purification of the metal had been effected by two depositions from a sulphate electrolyte and a third from a nitrate solution. The resulting cathode material was melted in a pure graphite crucible and final solidification in rod form was accomplished by extrusion of the melt through a water-cooled die surrounded by a reducing atmosphere. The analysis of this material, by a combination of chemical and spectrographic methods, was reported by the American

Smelting and Refining Co. as follows: Se not detectable; Te not detectable; Si, nil; Al, nil; Mg, nil; Fe, Ni, Sb, As, Pb, Ag, Bi, Sn, if present less than 0.0001. S, 0.0001 (max.) and O, 0.0004 (max.)* were determined by the authors.

The copper rods were surface-oxidized, according to previously described practice, and all specimens, except in the 650°C. treatment, were saturated in an atmosphere of nitrogen. The data of Table 1 and the plotted points of Fig. 1 indicate that any differences in oxygen solubility between this pure copper and the less pure O.F.H.C. material is negligible in comparison with the experimental error involved.

An opportunity was offered to make oxygen-solubility measurements on this high-purity copper to which 0.0219 per cent silver had been added to the melt by the American Smelting and Refining Co. That silver has little or no effect on the oxygen solubility is evident from the results assembled in Table 1 and Fig. 1.

An effort was made to locate some of the copper used by Rhines and Mathewson and we were successful in finding a number of specimens that had been used for their microscopic examinations. The copper had been in storage for almost seven years and naturally showed evidences of surface oxidation and sulphidation. After cleaning in a nitric acid solution the specimens were melted in a vacuum furnace to produce a slug weighing about 400 grams. This material was converted into chips, discarding the outer skin. In lots of about 100 grams the chips were charged into a combustion bulb and heated overnight at 950°C. in contact with a stream of hydrogen. The several residues were pressed into a slug, which then was melted in a vacuum furnace in a previously "burned-in" alundum thimble. An analysis of a sample taken from the ingot showed no measurable

concentration of sulphur and about 0.0006 per cent oxygen. It may be assumed that the material was then comparable from the standpoint of purity to its condition when exposed to saturation treatments by Rhines and Mathewson. From the cast slug, strips* (0.10 in. thick) were prepared and specimens subjected to saturation treatments. Our results on this material (Table 1, Fig. 1) are in good agreement with the data obtained on the other coppers.

DISCUSSION OF RESULTS

It is difficult to account for the significant differences in oxygen-solubility values made evident by a comparison of our results with the values given by Rhines and Mathewson. Experimental work of this nature requires constant vigilance in order to avoid contamination of the material, and and the final results are, unfortunately, based on analytical procedures that lack the necessary accuracy for the concentrations under test. Until more adequate determinative methods are available, all data relating to minute amounts of impurities in copper must be regarded with suspicion and at best accepted only tentatively. This viewpoint is most certainly adopted by the present writers, who will be the last to claim that the solubility limits indicated in this paper are final and irrevocable.

During the course of the investigation, an effort was made to obtain checks on our oxygen measurements by skilled operators in other laboratories. Unfortunately, the sensitivity demanded is distinctly beyond that required for routine analysis in the control laboratories of the copper industry and the research laboratories have not included this determination in their special analytical procedures. After the completion of our work, however, W. A. Baker, of the

* According to W. A. Baker of the British Non-ferrous Research Association, the superficial oxidation of low-oxygen copper introduces an error of 0.0002 per cent. This correction, however, has not been applied to any of our oxygen determinations.

* The writers are indebted to the American Smelting and Refining Company for the following analysis of the strip material: Fe 0.0008, Sb 0.0001, Pb 0.0003, Sn 0.00008, Ni 0.0002, Bi Nil, As Nil, Si Nil, Ag 0.1 oz./T.

British Non-ferrous Research Association, kindly consented to make oxygen determinations on some of our specimens. The method used by Baker has been described by him⁵ and consists essentially of heating the massive copper specimen in pure hydrogen under reduced pressure, condensing out the water vapor at $-80^{\circ}\text{C}.$, vaporizing the water in an evacuated system and determining the amount of oxygen by a measurement of the vapor pressure. Baker's values, together with the authors' determinations on duplicate samples are shown in Table 2. Although the two sets of quantitative results, based on distinctly different analytical procedures, are not in absolute agreement, they furnish supplementary evidence regarding the magnitude of oxygen solubility previously indicated by this work.

TABLE 2.—*Determinations of Oxygen by Two Investigators*
PER CENT

| Specimen, O.F.H.C. | Author's Determination | Baker's Determination |
|---|------------------------|-----------------------|
| Saturated 1600 hr. in air at $550^{\circ}\text{C}.$ | 0.0017 | 0.0008 |
| Saturated 73 hr. in air at $700^{\circ}\text{C}.$ | 0.0020 | 0.0010 |
| Saturated 35 hr. in nitrogen at $1040^{\circ}\text{C}.$ | 0.0068 | 0.0053 |

Assuming that Baker's results constitute a reasonably satisfactory confirmation of the oxygen-content measurements, it becomes necessary to look elsewhere for the explanation of the discrepancy between our results and those of earlier workers. It is, of course, obvious that incomplete saturation of the specimens could account for the lower values reported here. It may be stated in this regard that our shortest heating periods, as suggested by preliminary observations, were longer than we deemed necessary and the longer times adopted as a desirable precaution gave assurance that equilibrium had been attained. Furthermore, the saturation treatments satisfied the time requirements

as calculated from Ransley's⁶ diffusion data.

It is conceivable that the physical condition of the specimens used by Rhines and Mathewson may account for their higher values. Reference has already been made to the difficulty which they encountered in ridding the metal of the heavy scale, particularly after the treatments at high temperatures. The difficulty in accepting this observation as a satisfactory explanation of the discrepancy is obvious, however, when it is noted that in both investigations air served as the saturation atmosphere for temperatures up to about $900^{\circ}\text{C}.$, resulting, presumably, in similar scale formations. At the higher temperatures the nitrogen atmosphere undoubtedly furnished more satisfactory material for analysis and the differences in solubility for these temperatures could be explained adequately by the improved procedure for saturation. Still another consideration may be based on the surface condition that results from the rolling of a small ingot. Mathewson and Rhines used relatively small castings and it is possible that the rolled strip had an open texture due to a limited reduction of a cast material. The saturation treatment of such a strip would be accompanied by oxidation of minute fissures from which the oxide particles could not be removed by ordinary surface-cleaning methods.

Although it is common practice to subject experimentally derived constitutional data to further verification by supplementary experimental procedures, some attention has been devoted to the testing of such data on the basis of their conformity to thermodynamic considerations. Fink and Freche⁷ were conspicuously successful in showing that the experimentally determined solid solubility curves of several binary aluminum systems conformed to the laws of perfect solutions in that $\log x = -\frac{H}{RT} + C$. According to this equation, if the log of the atomic per cent of the solute

is plotted against the reciprocal of the absolute temperature a linear relationship must result if the solution behaves ideally.

In studying gas-metal equilibria, Borelius

intersecting lines better emphasize, and perhaps more clearly express, the deviation from linearity at temperatures above 925°C. It is also interesting to note that a

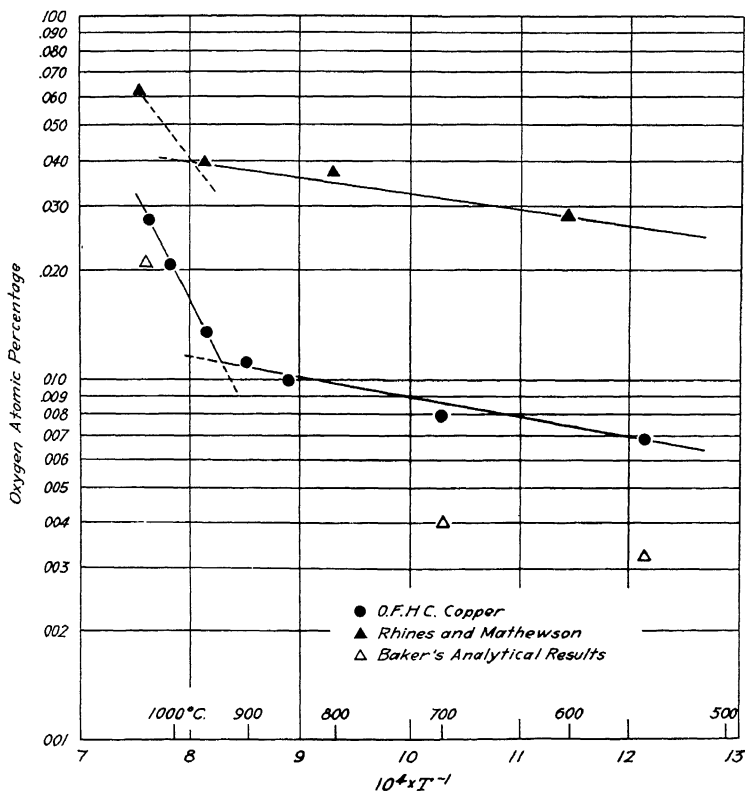


FIG. 2.—SOLID SOLUBILITY OF OXYGEN IN COPPER.

Log of atomic percentage of oxygen plotted against $\frac{1}{T}$.

and Lindholm⁸ plotted the results of Sieverts and his co-workers on a number of hydrogen-metal systems and, in each case, complete conformity to the linear relationship was observed. There is little evidence available in this regard on oxygen-metal systems, only for silver⁹ and cobalt¹⁰ has this relationship been emphasized.

This criterion has been applied to the solubility data of Table 1 with the results shown in Fig. 2. It is evident that the points do not lie on a straight line. Although it is possible to draw a reasonably smooth curve through the points, it is believed that two

plot of Rhines and Mathewson's results suggests a comparable deviation although their data furnished too few high-temperature values to be considered as other than possibly supplementary evidence. Again the analytical results reported by Baker—offering only three points, to be sure—fail to fall on a straight line. It is, of course, futile to discuss at this time the significance of these plots, since they are based on the questionable assumption that we are dealing with an ideal solution. Nevertheless, it may be suggested, but not stressed, that the point of intersection may indicate

a difference in type of solution above and below a critical temperature.

Although the present work is concerned primarily with the solubility relationships between copper and oxygen, it is realized that the several coppers used, relatively pure as they were, contained many impurities in varying concentrations. All of the metallic elements found in copper are capable of forming oxides and, with the exceptions of silver and any precious metals present, the oxides have higher free energies of formation than cuprous oxide and are, therefore, more stable than that oxide. Under the conditions for ensuring complete saturation of the copper, equally favorable conditions are attained for the internal oxidation of metal impurities. Rhines¹¹ has reported evidence of internal oxidation in about 35 copper alpha-solution alloys. When we realize, however, that the total metallic impurities of the special lot of American Smelting and Refining copper total less than 0.001 per cent, it is evident that even on the assumption that all of the potential oxides are absolutely insoluble in oxygen-saturated solid copper, considerably less than 0.001 per cent oxygen would be segregated as oxide and, therefore, not properly included in the oxygen content required for saturation. Obviously, any correction for the oxides present in high-purity copper may be considered negligible until more refined analytical methods are available.

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DISCUSSION

(E. M. Wise presiding)

J. S. SMART, JR.,* Barber, N. J.—I have had the pleasure of following the progress of the present work in the experimental stages, and am convinced that in this very condensed paper the authors have presented the results of an extremely laborious and skillfully conducted research. The excellent agreement obtained from coppers of diverse composition seems certain to negate the possibility of a relation between the oxygen solubility and the small amounts of impurities normal to commercial coppers.

The experimental method employed by the authors is one of long standing and proven worth for oxygen contents in the tough-pitch range. With the minute quantities involved in the present problem, however, meticulous care is essential to obtain even consistent results. In this, the authors have been conspicuously successful, and in all probability their results represent the present method at its best.

Unfortunately, the procedure involves the conversion of the sample to small chips having an enormous surface area, and there is no question that a measurable surface pickup is obtained. Heuer¹² found the effect to approximate 0.001 per cent O₂, and this would appear to rationalize the differences of 0.001 to 0.0015 per cent between the results of the authors and those of Baker (who uses the sample in the form of strip), were it not for the fact that Baker checked one of his determinations with chips and found the additional surface effect to be only 0.0002 per cent O₂. Consequently, it appears that the discrepancies may be partly dependent on a now obscure difference between the two methods, in addition to the superficial surface oxidation effect.

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¹² R. P. Heuer: *Jnl. Amer. Chem. Soc.* (1927) **49**, 2715.

Among the sources of difficulty, the purity of the reagent hydrogen appears due for more careful consideration than it has been given heretofore. The insertion of a palladium thimble in the hydrogen stream, and the use of a liquid-air trap, would certainly result in a considerable improvement over the usual purification train, while preliminary ignitions in carbon monoxide may provide access to the elimination of variable surface pickup.

From the evidence now at hand, it seems probable that the present oxygen solubility results, while much lower than those previously determined, are still slightly on the high side, probably by an amount that is nearly constant at all temperatures. It would also appear that the maximum deviation is about 0.001 to 0.005 per cent O_2 . The authors' results may be subject to such future correction, as they themselves suggest, but it is certain that the limitations of the present method must first be overcome, or a new procedure employed, if significant improvement is to be effected.

W. B. PRICE,* Waterbury, Conn.—On Fig. 1, the Raritan cathode shows consistently a larger volume of oxygen than the other types of copper, except at the end of the curve. This is particularly noticeable at 800°, where there is twice the amount of oxygen. Was the sulphur removed from the cathode, and if it was not might not the sulphur account for that increase in oxygen?

E. N. SKINNER, JR.—Mr. Smart's comments should be considered a very necessary corollary to this paper. As we have stated before, we feel that this method of analysis is severely burdened at these low quantities of oxygen. A method similar to that used by Baker which minimizes the adsorbed oxygen on the surface of the chemical sample would indeed be preferable. That there was always some adsorption was fairly evident since we were never able to prepare a copper that analyzed zero per cent oxygen. Furthermore, the appearance of copper chips after heating in hydrogen, as compared with chips machined from a solid strip which had been given a long-time hydrogen anneal, can be detected instantly by the difference in color.

As to the method of hydrogen purification, that, too, may be vastly improved. The use of a palladium thimble in conjunction with some system for freezing out residual impurities deserves consideration.

F. N. RHINES,* Pittsburgh, Pa.—An expression for the rate of internal oxidation of dilute copper alloys has recently been developed; this expression involves the solubility of oxygen in copper, which, if all the other variables are known, can be calculated by its use:

$$\frac{X^2}{t} = \frac{2D_o C_o}{B} \left(1 + \frac{C_o}{6B} \right)$$

where

$$B \approx \frac{C_o}{2} + C_m \frac{O}{M} \left(1 + \sqrt{\frac{D_m}{\pi D_o}} \sqrt{\frac{2}{3} + 2 \frac{O}{M} \frac{C_m}{C_o}} \right)$$

The depth of oxidation is x in time t ; D_o and D_m are, respectively, the diffusion coefficients of oxygen and the alloying element in copper; C_o is the solubility of oxygen in pure copper; C_m is the concentration of the alloying element; and O/M is the atomic weight ratio of oxygen and metal in the oxide formed. The rates of oxidation have been carefully measured in a large series of alloys and the other terms of the expression are well known, except C_o and D_o . Ransley has determined D_o in terms of C_o , so that the only value in doubt at the moment appears to be C_o . The approximate equality indicated in the second expression represents precision to the first two significant figures.

By substituting in this expression Phillips and Skinner's value and again Rhines and Mathewson's value and solving for $\frac{X^2}{t}$, which has been experimentally determined, a test of the validity of the two C_o values may be obtained:

$$\frac{X^2}{t} \text{ calculated from Phillips and Skinner's data} = 8.28 \times 10^{-7}$$

$$\frac{X^2}{t} \text{ calculated from Rhines and Mathewson's data} = 6.66 \times 10^{-7}$$

$$\frac{X^2}{t} \text{ experimentally determined} = 6.56 \times 10^{-7}$$

These values refer to a 0.103 per cent Si alloy oxidized at 1000°C., and are typical of a series

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of cases tested. If this method is valid (the indirect approach does leave some room for doubt), it indicates that the solubility of oxygen in copper is slightly higher than that reported by Rhines and Mathewson.

W. A. BAKER,* London, England.—In the footnote on page 305, I am loosely quoted as stating that “the superficial oxidation of low-oxygen copper introduces an error of 0.0002 per cent.” Actually, I pointed out that my analyses on massive samples gave figures lower than the authors’ results of analyses on chips, the difference being constant (within the probable limits of experimental error) at 0.001 per cent oxygen. I suggested that this was due to superficial oxidation, which would naturally be greater on the chip samples, and indicated that we had observed that superficial oxidation of a massive specimen of lead might introduce an error of 0.0002 per cent. There is a further source of error, which is also aggravated by the use of samples with a large surface area-weight ratio; namely, the adsorption of water vapor on the surface of the specimen prior to its insertion into the combustion tube. If the authors’ results are in fact consistently 0.001 per cent oxygen high from this source of error, the location of the solubility curve is materially different from that shown, the error being equal to more than 100 per cent at the lowest temperatures considered.

With regard to the disparity between the authors’ results and those of Rhines and Mathewson, it is conceivable that superficial oxidation and adsorption of moisture might account for the observed difference. It is worthy of note that whereas the authors weighed the chips and then introduced them into the ignition bulb with a minimum of delay, Rhines and Mathewson weighed the chips in the ignition bulb and, owing to the bulk of the latter, found it necessary to allow the sample and bulb to stand for an hour prior to final weighing. Any increase in weight due to adsorption of water prior to reduction was probably not compensated for by adsorption after reduction, since in the subsequent cooling period the chips were probably held in hydrogen, to avoid surface oxidation. The magnitude

of the error that might result from adsorbed moisture can be approximately estimated thus. We have determined the amounts of water vapor adsorbed on the surface of aluminum specimens and have found amounts of the order of 0.5 to 1 mg. per 100 sq. cm. Assuming that copper adsorbs similar amounts of water and that the chips used were, say, rectangular blocks, 1 by 1 by 2 mm., the surface area of 50 grams of such material would be of the order of 200 sq. cm. and the consequent error in the oxygen estimation by difference in weight could then amount to 0.004 per cent oxygen.

The writer is by no means sure that such errors account for the discrepancies noted, but it does appear that these sources of error should be carefully considered when making analyses for minute traces of oxygen.

A. PHILLIPS AND E. N. SKINNER, JR. (authors’ reply).—With respect to the method of saturation, we heated the specimens for periods that gave constant end points and considered the diffusion rates involved in connection with the evidence made available by the studies of Rhines and Mathewson and Ransley. We are not particularly concerned with the exact nature of the oxidized surface of the specimens; i.e., whether it consists essentially of CuO or Cu₂O, or both. The oxide surface simply served as a source of oxygen and there is abundant evidence proving that oxygen diffused to a constant concentration after heat-treatments extending beyond a given minimum time.

We are in agreement with Mr. Smart’s opinion that the present results are probably a little on the high side. We were particularly concerned with the error involved in the use of small chips for analysis and concluded that the error introduced could not be stated in absolute terms, but was highly dependent on the many conditions associated with the machining and handling of the chips.

Answering Mr. Price’s query regarding the higher concentrations shown for the Raritan copper, we do not believe that it is in any way due to the sulphur content, which was low. We have no explanation for the apparent difference in oxygen solubility between this copper and the other kinds and do not wish to place any emphasis on the implied difference.

Dr. Rhines has attempted an evaluation of our results and those previously published by

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Rhines and Mathewson based on a mathematical treatment of data furnished by studies of internal oxidation rates. We are unable to state at this time whether the agreement derived by inserting the Rhines and Mathewson data in the formula is conclusive or is, on the other hand, merely a coincidence.

We are somewhat puzzled regarding Mr. Baker's comments on the error due to superficial oxidation. In his original letter giving the results of his determinations on our specimens, Mr. Baker made the following statement: "Our analyses above were made on small strips

cut from the samples supplied, the sample being first freed from superficial oxide films with a clean file. Sample W₃ was also analyzed using chippings obtained by milling the previously cleaned strip. The chipping yielded 0.00099 per cent oxygen" (as against 0.00079 per cent for the cleaned strip). "The difference (0.0002 per cent) between the oxygen contents of the strips and chip samples from W₃ may reasonably be ascribed to superficial oxidation of the surfaces of the chips and it appears probable that your analytical results are consistently high to this slight extent."

Hydrogen Embrittlement of Pure Copper and of Dilute Copper Alloys by Alternate Oxidation and Reduction

BY FREDERICK N. RHINES,* MEMBER A.I.M.E. AND WILLIAM A. ANDERSON†

(Cleveland Meeting, October 1940)

THE investigations of Wyman¹ have demonstrated that copper deoxidized with several of the commonly used agents that confer immunity to ordinary hydrogen embrittlement can still be embrittled if it is annealed alternately under oxidizing and reducing conditions. During the oxidizing cycle, oxygen diffuses into the copper and frequently deposits a subscale composed of the oxide of the residual deoxidizing agent. Upon subsequent reduction with hot hydrogen, the copper becomes ruptured along the grain boundaries to a depth sharply limited by the previous penetration of oxygen as delineated by the inner boundary of the subscale.

Obviously the sensitivity to this kind of hydrogen embrittlement is engendered by the introduction of oxygen during the oxidizing anneal, but beyond this the mechanism of the process, and hence the controlling factors, remain obscure. There are several possibilities: (1) oxygen dissolved in the copper matrix of the subscale may, upon cooling prior to the hydrogen anneal, precipitate as cuprous oxide which is subsequently reduced by hydrogen as in the familiar case of hydrogen embrittlement; (2) oxygen in solid solution in copper may itself confer susceptibility to embrittlement by hydrogen; (3) the normally refractory oxides such as those of aluminum, silicon

and titanium may themselves be reduced by hydrogen when in contact with copper; or (4) the precipitated oxides of the subscale may be complex compounds such, perhaps, as $\text{SiO}_2 \cdot \text{Cu}_2\text{O}$, which are partially reduced by hydrogen. These possibilities have been examined, and it has been concluded that the first three and possibly the fourth are operative collectively or individually under more or less predictable conditions.

EFFECT OF PRECIPITATED CUPROUS OXIDE AND DISSOLVED OXYGEN

The literature provides no definite proof that oxygen in solid solution in copper can confer susceptibility to hydrogen embrittlement; indeed, the research of Leiter² seemed to indicate the opposite—that to produce the effect, cuprous oxide must be present in massive form and in a more or less continuous network along the grain boundaries. To test this point, pure copper has been annealed in hydrogen under conditions designed to ensure the presence in various samples of: (1) precipitated cuprous oxide, (2) dissolved oxygen only, and (3) no oxygen in any form. Very pure copper* said to contain no oxygen and no spectroscopically detectable traces of any other element (that is, no individual detectable impurity in quantity greater than 0.0001 per cent) was used. Strips of this material cold-rolled 75 per cent to $\frac{1}{8}$ in. in thickness were subjected to the following treatments, the results of which are noted:

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¹ References are at the end of the paper.

* Obtained through the courtesy of Dr. A. J. Phillips, of the American Smelting and Refining Co.

1. Embedded in a mixture of equal parts of cuprous oxide and copper powder, a bar was heated to 800°C. for 16½ hr. in an atmosphere of stagnant nitrogen, cooled in the furnace, and then reheated to 800°C. for 2 hr. in dry hydrogen. This specimen withstood only five right-angle bends before breaking, and upon microscopic examination was found to have a considerable number of moderately large holes along the grain boundaries (Fig. 1*b*). A section of this sample taken after oxidation and before the hydrogen treatment was found to contain a precipitate that exhibited the typical cuprous oxide color in its larger particles (Fig. 1*a*). In a similar experiment carried out at 1000°C. similar results were obtained; the specimen withstood less than one complete right-angle bend, and the microstructure showed the presence of numerous large cavities at the grain boundaries. Since hydrogen embrittlement begins at 400°C. and the sample was in contact with hydrogen while heating to 800°C., it is highly improbable that the precipitate was redissolved before embrittlement set in. This experiment is taken to indicate that the presence of precipitated cuprous oxide makes copper susceptible to hydrogen embrittlement.

2. Embedded in the copper-cuprous oxide mixture, another sample was heated to 800°C. for 45 hr. in a stagnant nitrogen atmosphere and then, without any lowering of the temperature, 2 hr. in dried hydrogen. This treatment should ensure the saturation of the copper with oxygen, and, since the temperature was not allowed to decrease between treatments, there should be no precipitate of cuprous oxide. The sample withstood 20½ right-angle bends before breaking; this is somewhat less than the breaking count for sound annealed copper. There were a number of small holes at the grain boundaries (Fig. 1*c*). Similar experiments in which the oxygen was introduced by first producing a thin scale on the copper instead of using a bed of cuprous oxide

powder gave similar results in treatments at both 800° and 1000°C. In some instances the embrittlement was more severe, and a few specimens withstood less than two right-angle bends. Apparently oxygen in solid solution in copper produces a mild susceptibility to hydrogen embrittlement.

3. Embedded in the copper-cuprous oxide mixture, another bar was heated to 800°C. for 45 hr. in stagnant nitrogen; then, without lowering of the temperature, 4 hr. in dry carbon monoxide; and, again without lowering of the temperature, 2 hr. in dry hydrogen. Ransley³ has demonstrated that pure dry carbon monoxide does not penetrate copper appreciably and will withdraw the oxygen from copper at a rapid rate without causing embrittlement; this sample should, therefore, be substantially free from oxygen before the hydrogen treatment. Various samples treated in this way withstood right-angle bends numbering as high as 33 before rupture. The microstructure was completely free from cavities of any kind (Fig. 1*d*); there has been no embrittling action.

4. A final sample was heated in dried hydrogen at 800°C. for 2 hr. The structure was perfectly sound, and the resistance to the bend test was of the same order of magnitude as that of the samples treated by procedure 3 above; i.e., the copper was not embrittled.

In summary, these observations indicate that a degree of susceptibility to hydrogen embrittlement is conferred upon copper either by oxygen in solid solution or by cuprous oxide precipitated from solid solution. The effect of the latter is evidently much the more severe. By heating in pure dry carbon monoxide, dissolved oxygen can be sufficiently withdrawn from saturated copper to destroy its sensitivity to hydrogen embrittlement. The copper used was not, in its initial state, embrittled by hydrogen.

The equipment employed in these experiments consisted of a fused silica tube fur-

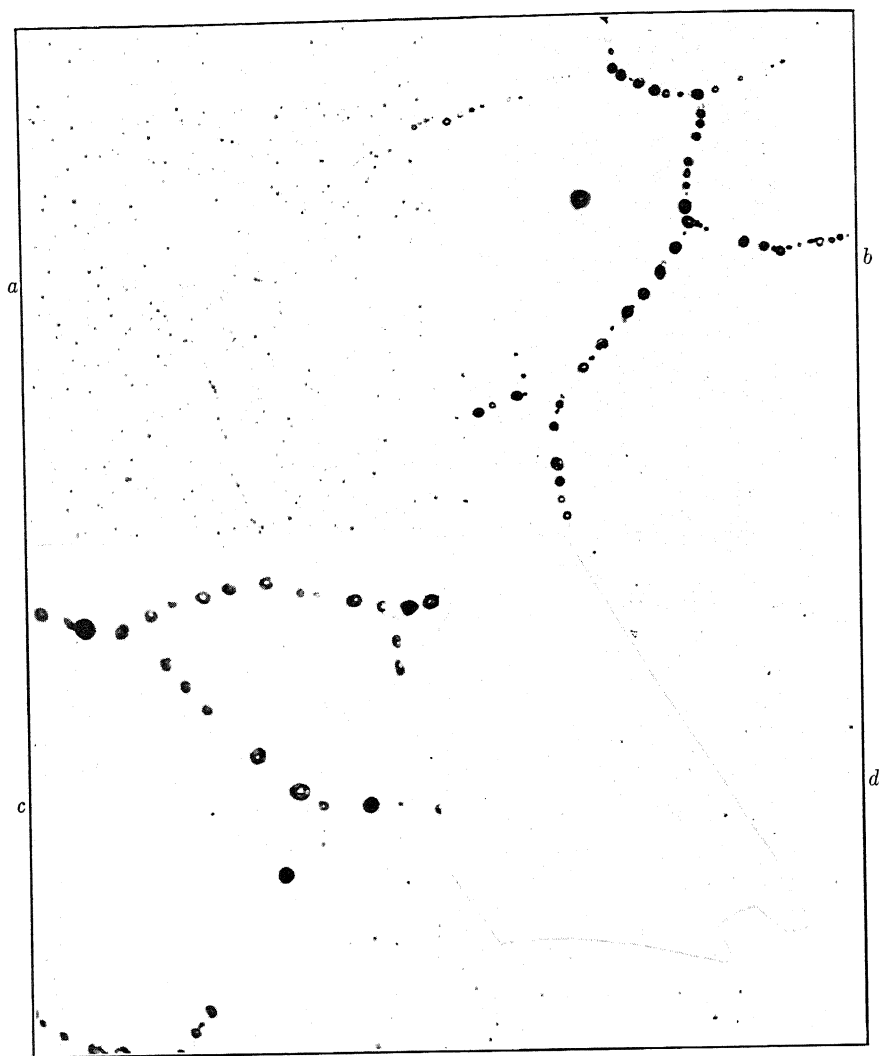


FIG. 1.—PURE COPPER.

a. Pure copper heated $16\frac{1}{2}$ hr. at 800°C . in a mixture of copper and cuprous oxide powder in a closed nitrogen-filled chamber; furnace-cooled. Shows a precipitate of cuprous oxide. $\times 500$.

b. Same as *a* reheated for 2 hr. at 800°C . in an atmosphere of dry hydrogen. Shows mild hydrogen embrittlement. $\times 250$.

c. Pure copper heated 45 hr. at 800°C . in a copper-cuprous oxide mixture in stagnant nitrogen, then without lowering the temperature, 2 hr. in dry hydrogen. Shows hydrogen embrittlement. $\times 500$.

d. Same as *c* but heated 4 hr. in pure dry carbon monoxide after oxidation and before introduction of the hydrogen. Shows no embrittlement. $\times 500$.

nace with a temperature controller. No metal other than the copper was introduced into the furnace; porcelain boats were used. Hydrogen was prepared by the action of hydrochloric acid upon zinc and was dried progressively with caustic soda, calcium chloride, and phosphorus pentoxide. Carbon monoxide was prepared by the dehydration of formic acid with sulphuric acid and was freed from moisture and carbon dioxide with soda lime, phosphorus pentoxide, and a liquid-air trap. The tank nitrogen used for neutral atmospheres was deoxidized by passing it over heated copper foil. The gas flow was never fast enough to alter sensibly the temperature of the furnace.

For the bend tests, a special vise was constructed. The lips of the jaws were rounded to a radius of $\frac{1}{16}$ in. and the protruding end of the sample was clamped to a pointer that moved over a protractor, so that the angle at which cracking or rupture occurred could be read within 5° of angle. The samples were bent first 90° in one direction then 180° in the opposite direction, and so on, each complete cycle being counted as four right-angle bends. Test pieces $\frac{1}{8}$ in. thick and approximately $\frac{1}{4}$ by 2 in. in area were used. This test, though crude, has been found by others to be very sensitive and, on the whole, a better indicator of the degree of embrittlement than more elaborate tensile measurements.

EFFECT OF FOREIGN OXIDES

A series of dilute copper alloys, originally made for a study of internal oxidation,⁴ was used. Cold-rolled strips of the original unoxidized alloys were cut into bars $\frac{1}{8}$ by $\frac{1}{4}$ by 2 in. and were subjected to three kinds of treatment: (1) embedded in a copper-cuprous oxide mixture, a set of alloys was heated 45 hr. at 800°C. in a closed chamber; (2) another set was heated in dried hydrogen at 800°C. for 2 hr. (the same treatment as paragraph 4 above);

and (3) a third set embedded in a copper-cuprous oxide mixture was treated successively at 800°C. * with stagnant nitrogen for 45 hr., pure dry carbon monoxide for 4 hr., and dried hydrogen for 2 hr., without at any time any lowering of the temperature (the same as treatment paragraph 3 above). The first treatment was designed to produce a subscale of the alloying element, the second to test the effect of hydrogen alone on the alloys in their initial state, and the third to produce a subscale and then to expose it to hydrogen after the removal from the copper of dissolved oxygen that might mask the effect of the precipitated oxides by itself inducing hydrogen embrittlement.

All bars were subjected to a bend test, the results of which are recorded in Table 1. Since the embrittlement was invariably limited to the zone of internal oxidation that usually extended only part way through the samples, the appearance of the first crack was a better indicator of embrittlement than the final rupture; wherefore, the angle of bend at which cracking was first observed has been recorded as well as the angle at rupture. When the sample was oxidized throughout, the first crack and rupture occurred almost simultaneously. The reproducibility of these results was remarkable despite the apparent crudity of the bend test and the variations to be expected in successive annealing treatments. Often the test results agreed within 5° of angle in successive experiments. The over-all precision is felt to justify reporting the results within one-half of a right-angle bend in the general case and to one-quarter of a right-angle bend when brittleness was extreme.

Table 1 shows that many of the alloys are embrittled to some extent by the

* All of the experiments reported here were carried out at a temperature of 800°C. because previous studies have shown that hydrogen embrittlement is often most severe at this temperature. Many tests run at temperatures of 900° and 1000°C. , not reported, have given entirely similar results except that the action is more rapid at the higher temperatures.

presence of the subscale itself. This is indicated chiefly by the early appearance of surface cracks. In some instances, that almost without exception the alloys seems to have imparted brittleness. The most pertinent observation, however, is that almost without exception the alloys

TABLE I.—*Summary of Results*

| Alloy Composition, Per Cent, Balance Copper | Internal Oxidation Only | | Annealed in Hydrogen Only | | Internally Oxidized and Annealed in H ₂ | | Type of Microstructure in Oxidized and Reduced Samples |
|---|----------------------------|---------|------------------------------|---------|---|---------|--|
| | Number of 90° Bends | | Number of 90° Bends | | Number of 90° Bends | | |
| | 1st Crack | Rupture | 1st Crack | Rupture | 1st Crack | Rupture | |
| 0.03 Al | 6 | 11 | 15 | 22 | 1½ | 2½ | III |
| 0.17 Al | 6½ | 8½ | 12 | 16 | 2½ | 5½ | IV |
| 0.03 As | 20 | 22½ | 1 | 1¼ | 2 | 2 | III |
| 0.05 B | 16½ | 17½ | 19 | 25 | 1½ | 1½ | II |
| 0.054 Be | 5 | 10 | 12 | 14 | 6½ | 9 | IV |
| 0.101 Be | 3 | 6 | 4½ | 15 | 2½ | 7 | IV |
| 0.03 Bi | 18 | 20 | 1 | 1¼ | 2 | 2 | III |
| Traces Ca | 10 | 12 | 3 | 23 | 1½ | 4½ | IV |
| 0.04 Cb | 12 | 20 | 12 | 17 | 1 | 1½ | V |
| Traces Ce | 4 | 16 | 16 | 20 | 1½ | 2 | III |
| 0.14 Co | 11 | 23 | 1 | 1 | ½ | 1½ | II |
| 0.10 Cr | 15 | 20 | ½ | ½ | 2 | 2 | II |
| 0.56 Fe | 4 | 6½ | 6 | 9 | 1 | 4½ | IV |
| 0.03 Ga | 18 | 21 | 12 | 12½ | 10½ | 11 | V |
| 0.25 In | 7 | 16 | 17 | 19 | 1½ | 1½ | I |
| 0.02 Li | 12 | 14 | 21 | 28 | 2 | 3 | V |
| 0.11 Mg | 4 | 7 | 15 | 24 | 1½ | 2 | I |
| 0.033 Mn | ½ | 25 | 12 | 15 | ½ | 1 | I |
| 0.22 Mn | 3 | 6 | 15 | 21 | ½ | 2 | I |
| 1.55 Mn | 3 | 8 | 16 | 19 | ½ | 8 | I |
| 0.115 Ni | 11 | 14 | 6 | 15 | 1 | 1 | I |
| 5 Ni | 2½ | 2½ | 16 | 17 | ½ | 2½ | I |
| 0.03 P | 9 | 10 | 11 | 16 | ½ | ½ | I |
| 0.24 P | 2½ | 10 | 10 | 14 | 1 | 12 | I |
| 0.42 P | 1½ | 6½ | 9 | 13 | 2½ | 7 | I |
| 0.03 Pb | ½ | 10½ | 20 | 26 | 1 | 15 | II |
| 0.03 Sb | 13 | 16 | ½ | ½ | ½ | ½ | III |
| 0.045 Si | 13 | 16½ | 20 | 23 | ½ | ½ | II |
| 0.180 Si | ½ | 2 | 3 | 14 | ½ | 8 | III |
| 0.858 Si | ½ | 4½ | 6 | 6 | ½ | 24 | III |
| 0.31 Sn | 6 | 11 | 2 | 2 | ½ | 2 | I |
| 0.1 Sr | 7 | 13 | 16 | 21 | ½ | ½ | III |
| 0.04 Ta | 4½ | 7 | 5 | 10 | ½ | 1 | III |
| 0.05 Ti | 8 | 13 | 5 | 7 | 1 | 1 | IV |
| 0.09 V | 9 | 10 | 9 | 17 | 1 | 2 | III |
| 0.21 Zn | 15 | 16 | 14 | 17 | ½ | ½ | I |
| 0.16 Zr | 6 | 12 | 12 | 18 | 5 | 6 | V |
| 0.03 Be + 9.52 Zn | ½ | 16 | 21 | 24 | 11 | 20½ | I |
| 0.13 Al + 9.29 Zn | 2 | 12½ | 17 | 20 | 1½ | 12 | I |
| 0.085 Si + 9.81 Zn | 1½ | 18 | 16 | 20 | 14 | 18 | I |
| 0.006 Be + 4.93 Sn | ½ | 16 | 19 | 20½ | 1 | 7 | I |
| 0.06 Al + 5.43 Sn | 2 | 8 | 17 | 21 | ½ | 12½ | I |
| 0.085 Si + 5.02 Sn | 1½ | 1 | 28 | 32 | ½ | 20 | I |

notably those of the alloys of arsenic, antimony, bismuth, cobalt, and chromium, the hydrogen treatment alone that were oxidized and then treated with hydrogen have been embrittled. The degree of the effect varies, and in general the

a. 0.21 per cent Zn; given treatment described under Fig. 1*d*. Type I embrittlement. Shows complete reduction of all zinc oxide at grain boundaries and within grains.

b. 0.05 per cent B; same treatment as *a*. Type II embrittlement. Grain boundaries open as continuous cracks, reduction of oxide within grains uncertain.

c. Traces Ce; same treatment as *a*. Type III embrittlement. Grain boundaries cracked open for short distances, elsewhere holes along grain boundaries.

d. 0.05 per cent Ti; same treatment as *a*. Type IV embrittlement. Holes along grain boundaries rarely connected by cracks.

e. 0.10 per cent Mg; same treatment as *a*. Type V embrittlement. Structure almost sound.

f. 0.085 per cent Si and 5.02 per cent Sn; same treatment as *a*.

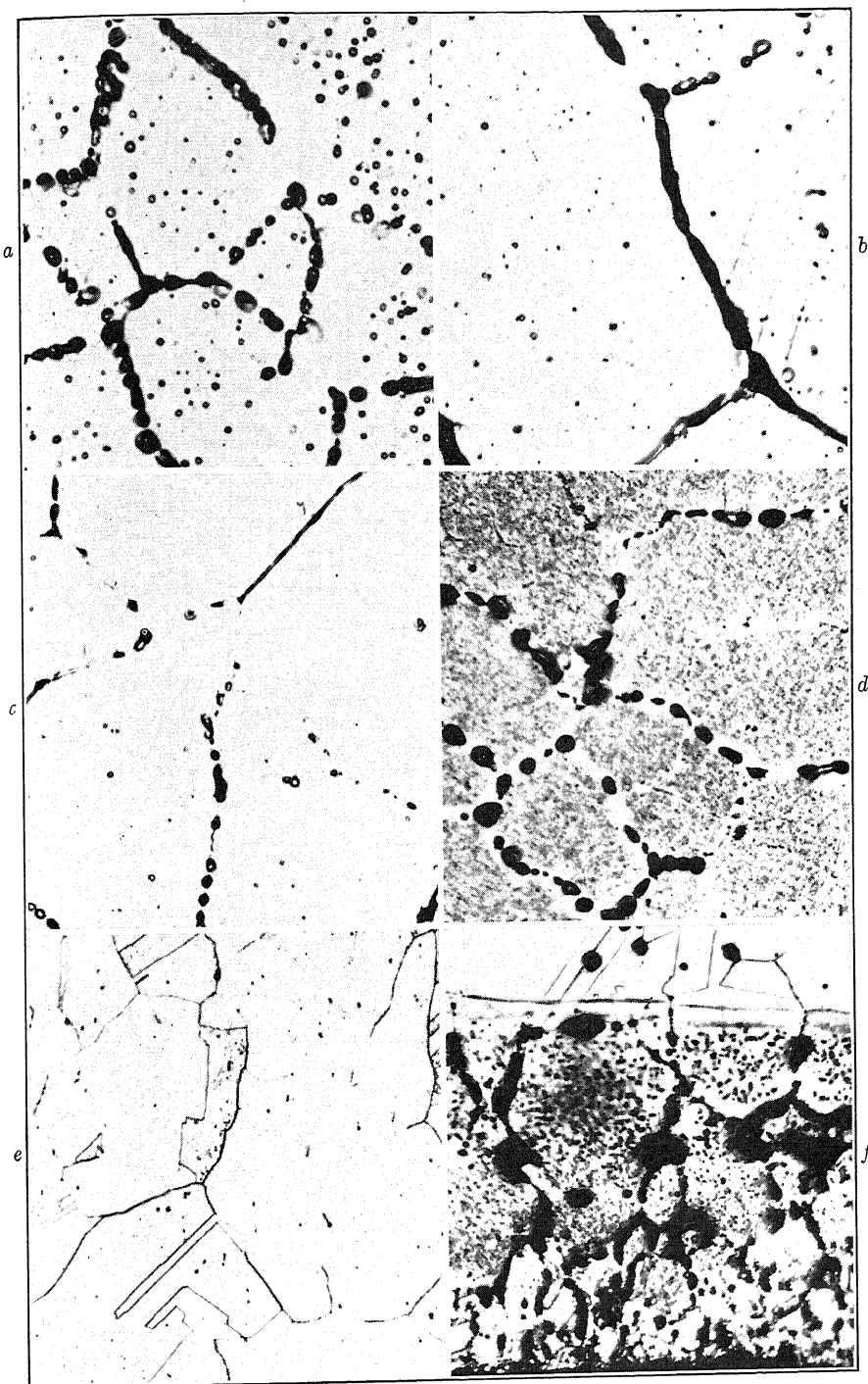


FIG. 2.—VARIOUS ALLOYS OF COPPER. $\times 250$.
[For descriptive legend see opposite page.]

alloys containing oxides known to be easily reduced by hydrogen are most affected, while those with the most refractory oxides are embrittled to only a minor degree.

These observations assume more definite significance when supported by the findings of the micrographic studies. Photomicrographs of many of these alloys in the oxidized condition have been published.⁴ The similarity among the microstructures of the alternately oxidized and reduced samples makes the reproduction of a complete pictorial record here unnecessary, but representative examples of the several general types are presented in Fig. 2, *a* to *e*; the various alloys are classified according to these type structures in Table 1. The Roman numerals used for designating the structural types indicate the following: (I) grain boundaries open throughout oxidized zone, oxide within grains appears reduced; (II) grain boundaries open throughout oxidized zone, reduction of oxide within grains uncertain because of small size; (III) holes and occasional channels at grain boundaries throughout oxidized zone; (IV) holes only at grain boundaries in oxidized zone; (V) no apparent discontinuities in the structure.

Among the alloys in which the oxide precipitate was everywhere reduced and in which the embrittling effect was most extreme are those containing indium, manganese, nickel, phosphorus, tin, and zinc. There seems to be every reason to believe that the hydrogen has reacted vigorously with the foreign oxides in these alloys, producing steam, which burst open the samples at the grain boundaries as in ordinary hydrogen embrittlement.

The oxide in the tin alloy has been definitely identified by X-ray diffraction methods as SnO_2 and that in the phosphorus alloy tentatively by indirect means as P_2O_5 . Thus it is certain that in the tin alloys a complex oxide is not required for this behavior. Oxides in several other alloys, not included in the above group in which reduction was certain, have also been

identified; these include SiO_2 , Al_2O_3 , Cr_2O_3 , Fe_3O_4 , Pb_3O_4 , TiO_2 , and ZrO_2 . Among the oxides not yet identified are several whose diffraction patterns are complex and do not correspond with those of any known oxide. These might be complex oxides in which copper occurs in addition to the alloying element.

At the other extreme is a series of alloys that suffered no visible structural change during the hydrogen treatment subsequent to oxidation—including columbium, gallium, lithium, magnesium, and zirconium. Even among these, however, there has been a slight decrease in the resistance to the bend test, and it is altogether possible that there were holes at the grain boundaries too small to be distinguished from the oxide precipitate.

Intermediate between these two groups is an almost continuous series in which embrittlement has definitely occurred, but to varying degrees. Least affected in this group are the alloys of aluminum, beryllium, calcium, titanium, and perhaps iron; more affected are arsenic, bismuth, cerium, antimony, silicon, strontium, and tantalum; and still more affected are cobalt, chromium, boron, and lead.

The alloys of manganese, phosphorus, and silicon are of particular interest, for they show the influence of the amount of the alloy element. Since all were oxidized under identical conditions, those with the lowest alloy content will have oxidized to the greatest depth. The first alloy in each of these series—that is, the one with the lowest amount of alloy addition—has been oxidized throughout, and in the bend test the first crack and final rupture occurred together. With larger alloy additions, there remained in the sample a core of unoxidized tough metal that caused the sample to withstand several right-angle bends between the appearance of the first crack and the final break. The appearance of the series of manganese alloys after oxidation and reduction is shown in Fig. 3.

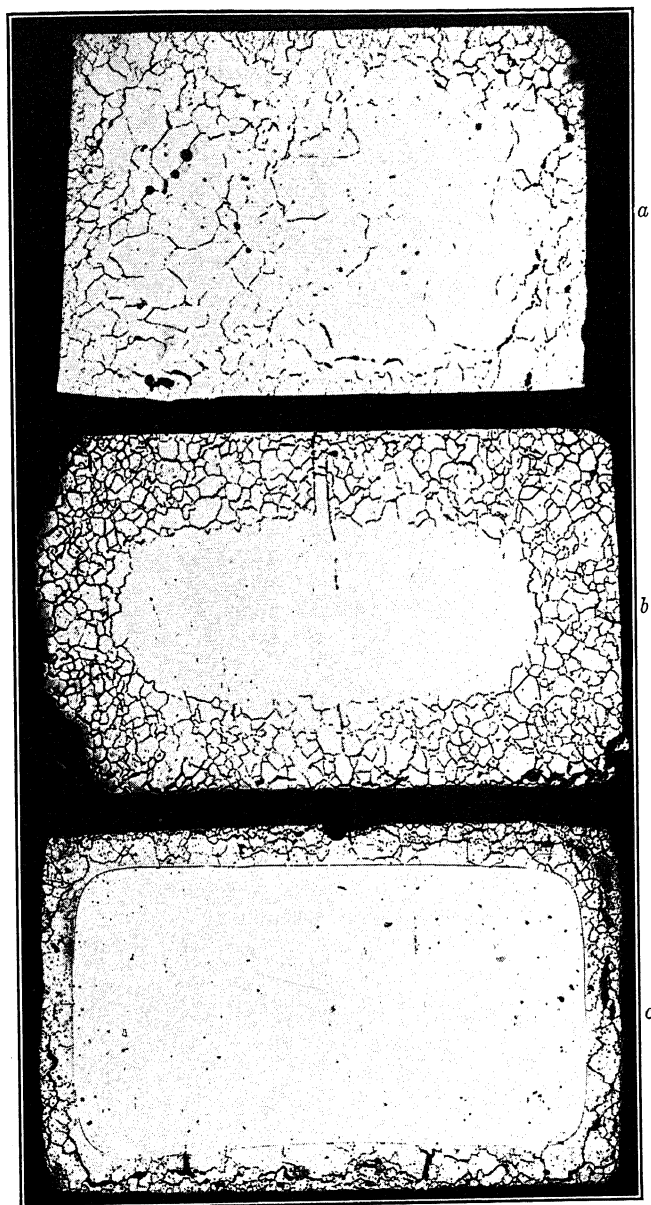


FIG. 3.—COPPER-MANGANESE ALLOYS. $\times 15$.

a, 0.033 per cent Mn; *b*, 0.22 per cent Mn; *c*, 1.55 per cent Mn.

Annealed 45 hr. in copper plus copper oxide powder, 4 hr. in carbon monoxide and 2 hr. in hydrogen without lowering of the temperature between treatments. The cracks formed by hydrogen embrittlement extend only to the limit of internal oxidation, the depth of which decreases as the alloy concentration increases.

The ternary alloys of zinc or tin with aluminum, beryllium or silicon all behaved similarly. Because of the high tin and zinc contents, these form a relatively thin subscale with a very heavy precipitate of the oxides. This zone was always thoroughly ruptured (Fig. 2f) by the hydrogen treatment and often split away from the unoxidized core at the interface spontaneously before the bend test. For this reason, some of the samples presented a new and unaffected surface and apparently were resistant to the bend test.

In a discussion of the internal oxidation studies carried out upon this series of alloys, A. A. Smith and J. S. Smart, Jr.⁴ pointed out that the presence of an impurity such as iron would probably result in the precipitation of a second oxide in addition to the oxide of the intended addition. These alloys were analyzed for iron, and it was found that detectable quantities were frequently present, the quantities ranging from barely detectable traces to a maximum of 0.03 per cent in the alloys containing beryllium and cerium. These experiments have shown iron to be definitely, though weakly, effective in causing susceptibility to hydrogen embrittlement. It is possible, therefore, that the slight embrittlement found among the beryllium and cerium alloys and two or three of the others, including in particular vanadium, may result from the iron impurity.

It is not unreasonable that a refractory oxide such as silica should be reduced by hydrogen in the presence of copper; indeed, it is well known that molten deoxidized copper will absorb silicon from a silica crucible. The copper simply provides a solvent for the liberated silicon, carrying it away from the reaction zone and thus permitting the reaction to continue with the accumulation of water until such a pressure is built up that an expanded cavity or open channel is blown in the copper. On this basis, it is to be anticipated that any oxide will be attacked to some extent, the

less refractory ones reacting the most vigorously.*

Pilling⁵ has described the hydrogen embrittlement of oxygen-bearing copper-nickel alloys where a eutectic of copper and nickel oxides occurs in the cast structure, and Bengough and Hill⁶ believed that a complex oxide of arsenic occurring in cast arsenical coppers leads to hydrogen embrittlement.

The action of hydrogen on several of the unoxidized alloys deserves special notice. Varying quantities of oxides were inevitably introduced into the alloys when they were cast and their presence may well explain the unexpected embrittlement of the calcium, cobalt and chromium alloys that exhibited typical cavities after the simple hydrogen anneal. The same explanation may apply also to the alloys of arsenic, antimony and bismuth annealed in hydrogen, but there is a further and perhaps more attractive explanation of the very pronounced effects found in these. It is improbable that the similarity in behavior among the members of this familiarly associated group of metals is accidental. Arsenic, antimony and bismuth each form several hydrides, among which are the well-known volatile compounds arsine, stibine and bismuthine. Such gases under pressure might well produce cracks and cavities in the copper, but there is as yet no proof of their formation in these alloys.

* If the alloys are arranged in the order of the free energy of formation per gram atom of contained oxygen in their respective oxides, they appear in approximately the same sequence as when arranged according to their susceptibility to hydrogen embrittlement; those with the largest negative values of free energy correspond with the highest resistance to embrittlement. The free energies of some are as follows: Cu_2O , -35150; MnO_2 , -51450; NiO , -51700; ZnO , -76000; SiO_2 , -95200; Cr_2O_3 , -98300; TiO_2 , -106400; Al_2O_3 , -119500; ZrO_2 , -122700; and MgO , -136370. The reaction is limited by the back pressure of the alloy element in solution in the copper, and much less magnesium in solution would be required to stop the reduction of MgO than would be required for nickel and NiO . Thus refractory oxides surrounded by an alloy containing sufficiently large quantities of the corresponding metal, such as might appear in a casting of aluminum bronze with alumina inclusions, may be immune to reduction by hydrogen. Also, where large quantities of oxides are present their reduction may proceed to a certain limit and then cease.

Although the observations reported here often referred to individual tests, the work has all been examined for reproducibility. More than three hundred samples were tested.

MECHANISM OF HYDROGEN EMBRIITLEMENT

The relationship between the conclusions drawn from this research and the theory of the hydrogen embrittlement of copper as it is understood today may perhaps be more clearly demonstrated by briefly summarizing the knowledge of the subject with the incorporation of the new observations.

At temperatures higher than 400°C., hydrogen will diffuse into copper containing cuprous oxide and will reduce the oxide to metallic copper and water vapor, leaving the metal ruptured along the grain boundaries.⁷ Hydrogen diffuses through copper much faster than the water vapor can escape by diffusion, and a pressure sufficient to rupture the metal is thus built up.⁸ The cracks and holes apparently occur at the grain boundaries, because of inherent weakness there, because of more favorable conditions for nucleation there, because the oxide is more plentiful there, or because hydrogen enters more rapidly at the grain boundaries; on the other hand, it is conceivable though less probable that rupture actually occurs randomly and the copper grains simply grow during annealing until limited by the discontinuities. Although several early investigations indicated that carbon monoxide and other reducing gases could embrittle copper, it is now known that hydrogen is the only gas (whether initially present in the gas or formed by reaction with water or hydrocarbons) that will produce this type of embrittlement in copper.^{1,3,7} The oxygen may be present in any or all of several forms: cuprous oxide deposited as a eutectic mixture at the time of casting or precipitated from solid solution after an oxidizing anneal, oxygen in solid solution, or oxides of other metals

embedded in the copper. The effect is most pronounced in cast copper, where the oxide is most concentrated and easily reduced, and becomes less pronounced as the oxygen is more homogeneously distributed, as in a solid solution, or when it is combined in a less easily reduced form as in the oxide of some alloying element. In all cases the rate at first increases with the temperature, and, except in cast copper, which shows a maximum at 800°C.,⁹ this increase continues at least to 1000°C. The log of the square of the depth of embrittlement in unit time is usually a linear function of the reciprocal of the absolute temperature.* The rate of embrittlement decreases gradually as the hydrogen pressure decreases; at very low pressures the rate of decrease is more rapid.⁸ Oxygen-free or deoxidized copper is not susceptible to embrittlement upon annealing in hydrogen,¹⁰ unless it has first been heated in an oxidizing atmosphere.¹ In this case, the rate of oxidation is much slower than that of the penetration of hydrogen, and except in very short reducing treatments the depth of embrittlement is controlled by the slower rate of internal oxidation. Hydrogen embrittlement varies in its severity both in the depth of penetration of the effect and in the size and degree of continuity of the ruptures produced. Cuprous oxide or dissolved oxygen may be withdrawn from copper to such an extent by heating in pure dry carbon monoxide⁹ that the susceptibility to hydrogen embrittlement is destroyed; foreign oxides are but slowly removed, if at all, by this method.

SUMMARY

The new results obtained in this study are as follows:

* This relationship has not been stated previously but can be derived from the data of Pilling,³ Wyman,¹ and several others. The results of any single investigator are usually self-consistent, but the discrepancies among the several rate studies reported in the literature suggest that the absolute value of the rate is subject to many variables, of which the distribution of the oxide is probably the most important. The decrease in the rate above 800°C. in cast copper has been ascribed to a welding of the cracks after the steam is released.⁹

1. It has been demonstrated that very pure copper can be made susceptible to hydrogen embrittlement by saturating it with oxygen. Embrittlement follows whether the oxygen is held in solid solution or is allowed to precipitate as cuprous oxide.

2. It has been demonstrated further that foreign oxides embedded in copper are reduced by hydrogen at elevated temperatures and that a type of hydrogen embrittlement can result from this cause alone.

3. The oxides known to be reduced in hydrogen, such as those of indium, manganese, nickel, phosphorus, tin, and zinc, produce the most severe embrittlement, while the oxides of columbium, gallium, lithium, magnesium, and zirconium are only slightly effective; intermediate in their effect are the oxides of aluminum, arsenic, beryllium, bismuth, boron, calcium, cerium, cobalt, chromium, iron, lead, antimony, and titanium.

4. A type of embrittlement less severe than hydrogen embrittlement is caused by the presence of a subscale on copper alloys. Subscales in which the oxide precipitate is heaviest or most concentrated at the grain boundaries are most damaging.

5. Copper alloys containing small quantities of arsenic, antimony, or bismuth were embrittled by annealing in hydrogen without previous oxidation. It is suggested that volatile hydrides such as arsine, stibine, or bismuthine may have formed under sufficient pressure to cause the rupture of the alloy.

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DISCUSSION

(W. H. Bassett, Jr., *presiding*)

A. PHILLIPS* AND D. B. GRAVES,† New Haven, Conn.—The production and increasing use of substantially oxygen-free copper has converted one academic query into a question of practical significance; namely, whether oxygen present in solid copper within the solubility limits renders the copper susceptible to hydrogen embrittlement. A study of this matter has been made at the Hammond Metallurgical Laboratory and the results to date substantiate the claim of Rhines and Anderson that embrittlement may be encountered without the presence of discrete particles of cuprous oxide.

In order to obtain conclusive evidence regarding the susceptibility to gassing of copper holding oxygen in solid solution, it is of course imperative to preclude the possibility of precipitation of Cu_2O after the saturation treatment and prior to, or during, the hydrogen treatment. This necessity has been properly appreciated by Rhines and Anderson and there is no reason to believe that precipitation of oxide had taken place within the specimens during the sequence of treatments. The authors did, however, hydrogen-anneal their specimens with a surface layer of oxide produced by heating in the copper-cuprous oxide mixture. As will be noted later, the present writers removed the surface oxide produced by the saturation treatment in order to eliminate any possible concomitant gassing effects at the surface.

The sequence of treatments observed at the Hammond Laboratory may be summarized as follows:

1. Oxidized surface in air to produce a visible coating.
2. Attained saturation by heating for 42 hr. in purified nitrogen.
3. Specimens quenched to prevent precipitation of cuprous oxide.
4. Scale removed by solution in dilute nitric acid.
5. Reheated in pure nitrogen to a temperature above the saturation temperature.

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6. Temperature adjusted to gassing temperature and specimen held at the temperature to ensure equilibrium conditions.

7. Passed in hydrogen to replace nitrogen. Heated in hydrogen atmosphere for 2 hours.

8. Hydrogen replaced by nitrogen and specimen allowed to cool.

The treatments were made on tensile-test specimens in order to establish a quantitative basis for studying hydrogen-embrittling effects. A typical set of our experimental results has been selected (Table 2) to confirm Rhines and Anderson's findings. It is to be noted that in the cases cited the hydrogen treatments were also carried on at temperatures above the saturation temperature and for this reason the results can in no way be attributed to the precipitation of cuprous oxide.

TABLE 2.—*Typical Results of Experiments by Phillips and Graves*

| Saturation Temperature, Deg. C. | Temperature of Hydrogen Treatment (2 Hr.), Deg. C. | Tensile Strength, Lb. per Sq. In. | Elongation in 2 In., Per Cent |
|---------------------------------|--|-----------------------------------|-------------------------------|
| 900. | No hydrogen treatment | 31,000 | 45 |
| 900. | 935 | 31,000 | 39 |
| 900. | 945 | 14,500 | 9.0 |
| 900. | 850 | 14,800 | 8.5 |
| 900. | 850 | 14,300 | 8.5 |
| 900. | 850 | 15,000 | 9.5 |
| 900. | 850 | 17,000 | 8.5 |
| 900. | 850 | 15,000 | 7.5 |
| 900. | 850 | 8,100 | 5.5 |
| 900. | 850 | 7,700 | 5.5 |
| No saturation treatment (OFHC) | Slowly heated to 900° in hydrogen and cooled in hydrogen | 29,900 | 34.5 |
| No saturation treatment (OFHC) | Slowly heated to 900° in hydrogen and cooled in hydrogen | 29,200 | 34.5 |

It is interesting to note the marked embrittlement of the specimens simply heated to 900°C. in hydrogen (after saturation) and allowed to cool in hydrogen. No surprise is occasioned, of course, by the observation that the treatment encouraging precipitation of oxide was associated with the maximum embrittlement, but rather by the evidence that gassing of copper containing only about 0.003 per cent oxygen can lower the strength from some 31,000 lb. per sq. in. to 8000 lb. and the elongation from over 40 per cent to 5 per cent.

S. ROLLE,* New York, N. Y.—Some years ago the Bell Telephone Laboratories did con-

siderable work on the hydrogen embrittlement of copper. As a result of their studies they standardized on 850°C. as the optimum temperature for heating copper in hydrogen to produce most rapid and pronounced embrittlement. I wonder whether temperatures above and below this were carefully explored and, if so, whether at elevated temperatures any healing action on fractures was noted.

E. E. SCHUMACHER,* New York, N. Y.—In the latter part of the 1920's we were interested in the use of an oxygen-free copper as a conductor in submarine cable. At that time a comprehensive study was made of the action of hydrogen on hot copper in connection with an investigation of means of producing oxygen-free or deoxidized copper. The degree of embrittlement by hydrogen of the various coppers tested was evaluated by the number of bends required to produce failure, together with tensile and ductility characteristics, after the specimens had been heated in hydrogen at 800° to 850°C. for periods of $\frac{1}{2}$ to 1 hr., depending upon the size of the specimen. The temperature of 800° to 850°C. was chosen because of the following considerations: Smith and Hayward, in 1926, and others had reported that the embrittling action of hydrogen on copper containing oxygen became pronounced at temperatures of 500° to 600°C., had its maximum effect in the region from 700° to about 850°C., and for temperatures above approximately 900°C. structural repair was initiated, which progressively increased in rate to the melting point of the copper. The rate of growth of the reduced zone for low-oxygen coppers, which were of interest to us, increased as the temperature was increased. These reported findings were spot-checked by us and confirmed. Consequently we chose a temperature for the embrittling treatment at which the penetration would be most rapid, but below the temperature at which the healing action commenced. The result was a choice of a temperature range of 800° to 850°C.

In answer to Mr. Rolle's question, we did observe a healing action at temperatures above 850°C. Specific results obtained on 0.032-in. dia. copper wire containing 0.03 per cent oxygen were as follows: Number of right-angle

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* Research Metallurgist, Bell Telephone Laboratories.

bends necessary to produce failure: (1) annealed in air 1000°C. for 1 hr., 9 bends, (2) annealed in hydrogen 800°C. for 1 hr., 1½ bend, (3) annealed in hydrogen 900°C. for 1 hr., 3 bends, (4) annealed in hydrogen 1000°C. for 1 hr., 6 bends. The treatment at the higher temperatures, where the embrittlement was less marked than at 850°C., resulted in considerable recrystallization and grain growth in the copper with the formation of new tight boundaries.

It was observed also that copper that had been treated with hydrogen at 1000°C. had sufficient ductility to permit subsequent cold-drawing and annealing. Following such a practice, a deoxidized copper with excellent ductility and freedom from embrittlement by reducing gases was produced.

S. ROLLE.—Our laboratory confirmed Mr. Schumacher's findings but not entirely with regard to the ductility of copper annealed in hydrogen at 1000°C. We found that this treatment "fully healed" the metal but its ductility was lower than that of metal that had not been so abused. As the result of Mr. Schumacher's and our investigation, we have standardized on 850°C. as the optimum temperature to heat copper in hydrogen to determine whether it is free from cuprous oxide and thus meet the specification which we have set up for OFHC copper.

W. R. HAMM.* State College, Pa.—In October 1939, a report was given¹¹ on the diffusion of hydrogen through oxygen-free copper. In connection with this work occasion was found to introduce oxygen and observe its effect on the hydrogen diffusion. The oxygen was introduced at 3-mm. pressure at 906°C., then helium was substituted and the temperature lowered in 1½ hr. to 650°C. At this temperature hydrogen diffusion was tried and was found to be identical in rate with that before oxygen was put in solution. That oxygen was really in solution in large quantity was evident, because when the temperature was raised to 792°C. the hydrogen diffusion was much above normal and the diffusor presently became porous, and could not be recovered by high-temperature treatment in vacuo. This meant to me at that time that at 650°C. and lower temperatures lattice diffusion of oxygen does

not take place, but somewhere between 650° and 800° it does begin and the usual combination with hydrogen at the grain boundaries occurs. However, other explanations have been offered.

I wish to ask the authors whether anything in their work indicates a fairly sharp lower limit for lattice diffusion of oxygen through copper.

L. L. WYMAN,* Schenectady, N. Y.—Clarification of several points would greatly enhance the value of this presentation.

The anomaly presented by the Leiter experiments apparently shows that the cuprous oxide must be in massive form to foster embrittlement when hot and subjected to hydrogen. This is somewhat misleading, to the extent that the special annealing treatment used by Miss Leiter was effective only in very thin sections of copper, and, consequently, the conclusions drawn in the Leiter paper cannot be considered as generally applicable. Thus it may be concluded, as the authors point out, that either dissolved or precipitated cuprous oxide can contribute to the embrittlement.

The subject of the blowing open of the grain boundaries by the embrittling action of the hydrogen must be interpreted in the light of our present concepts of what constitutes a grain boundary, for we may consider that during the oxidation of an oxygen-free copper there is more atomic "room" and activity in the grain boundary for precipitation than in the grain itself. Consequently, it might be expected that initial precipitation would occur in that location, which would account for Fig. 1c.

Similarly, it should be expected that, with a uniform oxygen distribution, the grain boundaries would be blown open before the grains themselves could be ruptured, because at these test temperatures the metal is considerably above both the recrystallization and equicohesive temperatures; thus the boundary is the weaker. Also, the boundaries blown open were probably those determined by the 1000°C. treatment; not those of the 800°C. test. This should be evident from the past work on the embrittlement of tough-pitch copper wherein embrittlement depths have been measured by the line of demarcation between reduced and unreduced oxide particles, irrespective of loca-

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¹¹ *Jnl. Chem. Phys.* (Oct. 1939) 7, 903.

* Research Metallurgist, General Electric Co.

tion in grain or in boundary, because no definite difference has been established between the action in these two regions.

The several types of embrittlement structure are of considerable interest, inasmuch as these were all produced at the same temperature and give some measure of what might be termed the "force" of the rupturing, and show this to be different for several addition agents.

The change in the types of ruptures was mentioned and discussed with reference to the different embrittlement temperatures in the series of papers by the present writer to which the authors have already referred, and these breaks in the rates may be due to similar actions in both cases. The presence of mixed or compounded oxides in these oxidized alloys (the CuPO_3 , CuAs_2O_4 , etc., identified by Fröhlich) may well foster unexpectedly rapid reductions in hydrogen in a manner comparable to the reduction of chromium oxide in the presence of nickel recently described by Grube.

It is noted that ZrO_2 is included among the materials in which reduction was certain, and some vestige of this might be expected. However, the authors state that there is no change during the hydrogen treatment subsequent to oxidation with zirconium added. Further explanation of this would be advantageous.

It is to be hoped that this work will be continued, the quantitative value being enhanced by improved technique in melting and alloying practice as well as by the inclusion of pure copper "blank" samples throughout.

F. N. RHINES AND W. A. ANDERSON (authors' reply).—The question as to whether or not oxygen in solid solution in copper can impart susceptibility to hydrogen embrittlement has been discussed inconclusively for so many years that it is indeed gratifying to find the very careful work of Phillips and Graves in such close agreement with our own. As a matter of interest, our specimens oxidized in cuprous oxide when cooled to room temperature in situ showed no visible evidence of an oxide scale; they had the typical pink color of fully reduced copper.

The embrittlement temperature of 850°C . was chosen with Smith and Hayward's observations in mind. A few samples were heated in hydrogen to 1000°C . and the embrittlement proceeded more rapidly, as was to be expected, but no marked healing effect was observed. This may be because complete rupture of the grain boundaries was uncommon in the samples that were free from massive cuprous oxide, and the embrittled structure thus resembled the "healed" structure in more severely ruptured copper.

We have done too little work on hydrogen embrittlement at the lower temperatures to have any clear idea of whether the mechanism of the effect is there essentially different. We do have data, however, upon the course of internal oxidation at 600°C . that shows that at this temperature the oxygen enters the copper chiefly at the grain boundaries, while at 750°C . diffusion of oxygen occurs generally across the grains. This seems to confirm Professor Hamm's observation.

Coalesced Copper—Its History, Production and Characteristics

BY H. H. STOUT,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1940)

IN the early fall of 1925, the writer was conducting, in the Ledoux and Co. laboratory, New York, experiments directed toward ascertaining the effect on its impurity content when cathode copper was subjected to a current of various gases at an elevated temperature below the melting point. The apparatus consisted of a vertical 1-in. dia. silica tube about 12 in. long, heated on the outside. The cathodes were broken to pass $\frac{3}{8}$ -in. mesh, and a current of various different gases was passed up through a 4-in. long column of these loose cathode particles in the vertical tube furnace. Temperature was maintained to 1500° to 1600°F. and the gas treatments lasted from 3 to 6 hr. The writer observed that whenever reducing gas (H_2 or CO) was used, these cathode particles stuck together at points of contact with each other. The cohesion was so marked and tenacious that an examination was made of the fractured surfaces, when cathode particles were broken from the cluster. Crystal growth was always found to have taken place across the surfaces where separate particles were in contact, but only after all oxides, sulphates, etc., had been completely removed. The idea of a possible new process was then conceived and was disclosed to A. M. Smoot (V. P. Ledoux and Co.) with intent to obtain his views. The first conception as given Smoot was "to gas-clean broken cathodes, put them in an extrusion press, solidify and extrude them at around 1500°F." Smoot's reaction, after a few moments considera-

tion, was, "It looks perfectly all right to me."

The writer and his assistants, W. H. Osborn and H. H. Stout, Jr., after conferring as to ways and means, decided to go ahead with preliminary laboratory experiments, which, it was thought, would move the new process from the possible to the probable. This program followed a course indicated by three basic considerations:

1. Since brittle cathodes were often unintentionally produced, it seemed probable that the laws controlling this type of deposition could be ascertained.

2. We had already proved the gas-cleaning feature.

3. There remained to prove: whether a sound, homogeneous metal billet could be produced with crystal growth established over the entire surface of each individual particle in the billet; and, if so, what would be the physical properties?

Osborn arranged with Columbia University for conducting experiments in its research laboratory to prove or disprove the third item; Columbia assigned C. A. Phillipi, Jr. to assist in the project. A press with a cylinder 2 in. high and of 1-in. dia. was used. It was surrounded and heated by a resistance coil of Nichrome wire. Broken tough cathodes were used.

EXPERIMENTAL PROCEDURE

The first run took place March 18, 1926. The resistance wire gave out when temperature of 1004°F. was obtained. Pressure was immediately applied: perceptible ram movement stopped when 39,000 lb. per sq. in. on the copper was reached, with a maxi-

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mum final pressure of 50,000 lb. per sq. in. The resulting billet (one-half shown as Fig. 1) was approximately 1 in. in diameter, $1\frac{1}{16}$ in. high and weighed 77.4 grams.

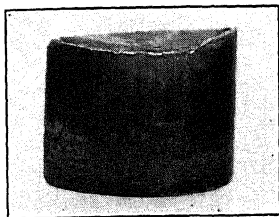


FIG. 1.—HALF OF FIRST COALESCED BILLET.

There were no gas pockets, but crystal growth had occurred across the original cathode-particle boundaries only in a few scattered spots (one of which is shown in Fig. 2). The fact that crystal growth had actually occurred gave definite proof of the fundamental metallurgical concept involved. The other half of the billet was heated, hammered to a spike, drawn, annealed and gave the following results when tested: sp. gr., 8.94; tensile strength soft 34,560 lb. per sq. in.; conductivity (I.A.C.S.), 101.1 per cent; twists in 6 in. to break, 64.

Three more runs were made with an improved resistance heating coil and all these resulted in complete crystal growth in every portion of the billet, as far as could be observed, with physical properties substantially the same as the first billet. The incomplete crystal growth in the first billet was thus proved to have been due to the lack of time and/or temperature caused by apparatus failure. No gas pockets were found in any of the billets. These results settled the determination to recommend proceeding with the new development, which was approved forthwith.

In order to give the reader a fairly good picture of what occurs in the new process, since it is quite revolutionary, a description of the underlying principles, as written in 1926 by W. H. Osborn, is given here:

Every solid piece of metal is composed of a mass of individual crystals in a state of balance

or equilibrium. If such piece of metal is hammered or bent or distorted in any way, the crystals are put under a strain, i.e., their balance or equilibrium is disturbed. If the metal is



FIG. 2.—PORTION OF FIRST BILLET. $\times 75$.

then heated, the strain on the individual crystals will be relieved by the shifting of crystal growth in new directions until a state of balance or equilibrium is restored. The individual crystals grow in size, large crystals absorbing smaller ones, during this period of realignment. We have found that when the surfaces of two separate pieces of copper were cleaned of all impurities and then brought into contact by pressure, which put the crystals of each piece under a strain, the application of heat to these particles not only relieved the strain by causing new directions of crystal growth within the particles, but also, there being nothing but copper to copper contact between the particles, permitted crystal growth to extend right across the old boundaries so that the two pieces became a single piece of metal, composed, like all single pieces of metal, of an aggregate of individual crystals. This growing together of the two particles we have termed *Coalescence*.

The further development of the process proceeded by orderly stages. First, a test unit was assembled, the main feature of which was an old wood-veneer press of about 150 tons capacity, with a triplex pumping unit. Both were in their dotage. Broken cathode particles were placed in an

8-in. outside diameter tungsten-steel cylinder with a 30-in. long 3-in. inside diameter bore. As in the first and smaller experimental setup, it was placed upon the platen of the press, heated by a surrounding tubular resistance furnace, and hydrogen gas was admitted at the bottom. It was closed at the top by the tip of a 30-in. long plunger fixed to the upper platen of the press. With a pressure of 33,500 lb. per sq. in. on the copper at about 1400°F., a 7-in. long solid copper billet resulted, weighing about 17 lb. A quarter section of this billet, hot-forged and drawn to No. 12 B. and S. wire, had the following characteristics:

Ten. str. (hard), 63,900 lb. per sq. in.

Elongation in 20 in., 0.8 per cent.

Twists to break in 6 in.:

Hard, average 98.

Annealed, average 101.

Conductivity, per cent I.A.C.S., annealed:

Maximum, 102.0.

Average, 101.65.

Again the metallurgy and quality of the copper were demonstrated, but practical difficulties developing during further trials led progressively to two major mechanical modifications:

1. A preliminary cold-briquetting operation was added in order to reduce the large length-diameter ratio of the coalescence cylinder, which previously had been required by the relatively large bulk of the cathode particles.

2. A separate furnace for heating and cleaning the briquetted cathodes was installed, contiguous to but thermally and mechanically independent of the coalescence container.

The first modification presented no difficulty whatever. The second was achieved experimentally by superimposing an especially designed tubular briquette heating furnace upon a now smaller (3-in. bore by 6 in. deep) separately heated tungsten-steel coalescence chamber through which hydrogen gas passed to the furnace above. When ready to coalesce, the red-hot briquette,

released by suitable means, dropped into the preheated coalescence chamber. The furnace was immediately removed without interrupting the protective flow of hydrogen gas, a preheated dummy block and plunger were inserted and pressure was applied to coalesce and extrude. Sound copper of excellent physical characteristics resulted. This method proved mechanically and thermally feasible and was used with minor adaptations in the design of the pilot plant that followed.

The pilot plant made use of a 2000-ton lead press in the plant of the Watson-Stillman Co. at Aldene, N. J. This pilot unit produced briquettes 9 $\frac{3}{4}$ in. long of 5 $\frac{3}{4}$ -in. dia., weighing about 67 lb. Subsequently these were heated and then simultaneously coalesced and extruded into 2 $\frac{1}{2}$ -in. dia. copper billets, at temperatures around 1450°F. in the copper and 700°F. in the coalescence container, with a maximum pressure of 60,000 lb. per sq. in. on the copper. The billets were successfully worked by commercial processes into tube, wire, rod and strip, the physical characteristics of which duplicated or bettered previous results. Sufficient mechanical and thermal data having been obtained, the final commercial plant was designed and constructed to handle a 9 $\frac{3}{4}$ -in. dia. briquette 16 in. long, to weigh in the neighborhood of 300 pounds.

PRODUCTION OF BRITTLE CATHODES

A concurrent research program on brittle cathodes, fully as arduous but less spectacular than the one just described, produced the desired product and uncovered the laws underlying its control. The technique of brittle-cathode production was found to be readily adaptable to standard commercial multiple tankhouse practice. A portion of a standard multiple-system tankroom is protected against dust entering from the casting department or other sources and is (for a tankroom) fairly free from dust. On the

usual crane rack are hung $\frac{1}{8}$ -in. hard-rolled copper sheets, soldered to the cathode rod, resembling standard blanks used for the deposition of starting sheets. The crane

posited crystal, as it grows, will be coated by a film of the agent. It is thus prevented from sticking too tenaciously to the blank, as well as from sticking too tenaciously to

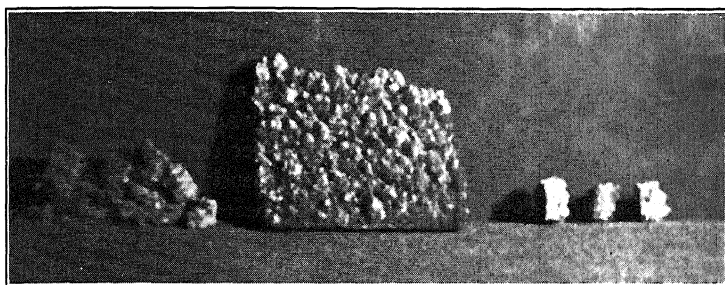


FIG. 3.—BRITTLE CATHODE SLAB AND HAND-BROKEN PIECES.

lifts the loaded rack, lowers it into and shortly thereafter raises it out of a tank filled with a solution of the embrittling agent in a mixture of gasoline and carbon tetrachloride (the last for fire protection). The room temperature and density of the solution determine the amount of embrittling agent that remains on the surface of the blank. If too much film is put on the blank, the deposit will be so brittle it may slough off, and conversely, if too little film is present, the deposit sticks to the blank and requires excessive labor to strip. The crane then carries the rack of filmed blanks and lowers it into the usual standard depositing tank. All the details of electrolyte composition, current density, anode spacing, circulation, temperature, inspection, chlorine control, etc., are the same as in standard multiple-system practice. Glue, however, is omitted from the electrolyte because of its toughening effect upon the cathode deposit.

The film of embrittling agent must possess sufficient dielectric strength to force the electric current to pierce it at separate individual points, at each of which the deposition of separate nuclei begins. The film must also possess sufficient selective wetting power for copper above that of the electrolyte so that each individual de-

the adjoining crystals, as by continued deposition they grow and touch each other. The best of these agents seem to be those containing unsaturated hydrocarbons. Corn oil and asphaltum give excellent results, but the latter must be free of silica ash. (Asphaltum, free of silica, may also be applied in emulsion form.)

Passing to a tank being pulled, the crane will lift a rack of blanks with the brittle cathode deposit on each side; and carry it to a standard washing platform, where water at 180°F . and 100-lb. pressure is applied in the usual manner. The deposit is then stripped from the blanks. If proper technique has been employed in applying the embrittling agent, a sharp rap with a hammer will be sufficient; if the technique has been lax, the stripping requires use of a hard-drawn copper spud. Fig. 3 shows the electrolyte side of a slab of brittle cathode and a pile of hand-broken pieces of the cathode. The stripped cathode falls upon and through a hard-drawn copper grizzly with 4-in. openings and into a copper-lined bin, from which it goes by belt conveyor to an automatic weigher which, in turn, feeds the briquetting press, subsequently described.

Summarizing the differences in the tank-house process of making brittle versus

tough cathodes, we have (when using Baltimore groove for both):

To the credit of brittle cathodes:

1. Starting sheets are not required.



FIG. 4.—SMALL BRIQUETTE.

2. From 15 to 25 per cent of direct current power for deposition is saved, because of the omission of glue, the use of a soldered contact between blank and cathode bar in place of the usual cathode loop and the absence of short circuits, which are caused by curling or distortion of starting sheets, etc.

3. No interest on starting sheets in process and in stock.

To the debit of brittle cathodes:

4. The application of the embrittling agent.

5. The stripping of the product from the blanks.

6. The interest and amortization on the rolled copper blanks.

BRIQUETTING

The automatic weigher discharges into a vertical briquetting press operating at room temperature. It is equipped with a $9\frac{3}{4}$ -in. dia. bottom plunger hydraulically actuated and a vertically floating container which, by friction, moves up over a static top plunger during the briquetting stroke. The

top plunger is moved out of the way by an auxiliary cylinder to permit the upward ejection of the finished briquette by the bottom plunger, and to admit a fresh cathode charge. The press is rated at 1250 tons, or about 33,500 lb. per sq. in. on the end of the briquette, which is $9\frac{3}{4}$ in. in diameter and 16 in. long. The particles preferably are compressed to a density of 83 ± 2 per cent of that of solid copper; greater density retards subsequent cleaning-gas penetration and lesser density does not give the required bonded strength. The length of the briquette should not exceed 1.6 times the diameter, otherwise, owing to friction, the ends may exceed 85 per cent density and the center may be insufficiently bonded to hold together during passage through the furnace. Fig. 4 shows a small briquette illustrating the general appearance of the copper mass ready to enter the furnace.

HEATING AND CLEANING

The finished briquettes are discharged from the press onto specially designed heat-resisting alloy-metal carriers, upon which each individual briquette remains out of contact with the adjacent briquettes (otherwise they would stick together in the furnace). These carriers, each in contact with the next, are pushed on tracks through the furnace by means of hydraulic cylinders, located outside the furnace but with pistons that enter the furnace through close-fitting openings in the wall. A more or less standard type of heating furnace is used, the difference being that it is more heavily insulated, is sheathed on the outside by welded sheet steel, and has tight-fitting doors, so that the furnace can be operated under a small positive pressure to prevent intake of air. Either gas (previously sulphur-cleaned) or electricity may be used for heating. The purifying gases must contain hydrogen and/or carbon monoxide. They are present in relatively small amounts, together with a comparatively high percentage of water vapor. This mix-

ture can be obtained by the use of hydrogen and steam; or by the carefully controlled partial combustion of low-sulphur fuel gas, the combustion gases from which contain H_2 -CO- H_2O - N_2 -CO₂, etc., and to which additional steam may be added if necessary. The briquettes remain in the furnace a minimum of 3 hr. and reach a temperature around 1550°F. The gas treatment removes any oxygen present, the great bulk of the sulphur and about 15 per cent of the arsenic and antimony, as well as eliminating any residual embrittling agent that may have escaped the hot-water washing.

TRANSFERRING, COALESCING AND EXTRUSION

In order to prevent reoxidation of the copper particles, the heated briquettes are transferred from the furnace to the extrusion press in the same atmosphere that is used in the furnace. This is accomplished by an auxiliary hydraulic cylinder, which pushes the briquette, still on its alloy carrier, out of the furnace through a gas-tight metal housing, into the sealed loading chamber of the extrusion press. The extrusion-press ram then pushes the briquette off its carrier and into the container of the press for coalescence and extrusion. Dummy blocks are supplied and alloy carriers are removed by auxiliary mechanisms. A conventional extrusion press is used except that, as described above, it is provided with means for the atmosphere-controlled transfer. The pressure per square inch on the face of the 10¼-in. dia. dummy block varies from about 20,000 lb. when extruding products with 15 sq. in. cross-sectional area up to 78,000 lb. when extruding products around 0.6 sq. in. cross-sectional area. If the extruded section is of large diameter, it is sawed to length. Flats and small rods are coiled hot. From this point on, the product is handled according to standard practice. Continuous extrusion can and has been accomplished: by this is meant that, by omitting the dummy block, crystal

growth will take place between the stub of each extrusion remaining in the press and the forward end of the succeeding briquette. This, however, occasions such high temperatures on the head of the ram, in the die and in the container that it will probably not be commercially feasible until and if a new alloy metal is discovered which will stand up under the resulting high temperatures.

CHEMICAL ANALYSIS

Table 1 gives the analysis of anodes from which were produced tough and brittle cathodes, from which, in turn, were produced respectively the wirebar and coalesced copper shown. For comparison, the analysis of OFHC copper is given as published by Webster, Christie and Pratt.*

At this point it may be stated that minimizing cathode contamination from anode substances other than copper constitutes an exacting requirement in the deposition of all cathodes in every system. The problem is somewhat increased in connection with brittle cathodes, since none of these substances are removable in a slag corresponding to that formed when tough cathodes are melted and refined (except such portions of these substances as are removed by the 1500°F. gas treatment, to which the brittle-cathode briquette is subjected in the coalescence process).

The minimizing of cathode contamination involves, among other precautions, the control of anode slag entrainment, the use of zinc oxide or other suitable electrolyte-soluble compounds for the anode mold wash, as well as prevention of dust contamination throughout the process. It also requires skillful control of all deposition functions in order to minimize contamination by electrolyte-insoluble anode impuri-

* W. R. Webster, J. L. Christie and R. S. Pratt: Comparative Properties of Oxygen-free, High-conductivity, Phosphorized and Tough-pitch Coppers. *Trans. A.I.M.E.* (1933) 104, 166.

ties, which settle down by gravity, through the liquor, into the slimes.

The omission of glue, as is to be expected, makes the face of brittle cathodes less smooth than the face of tough cathodes and

PHYSICAL PROPERTIES

Curves are available to the writer, showing in detail the comparative physical properties of coalesced and other coppers.

TABLE I.—Analysis of Anodes
PER CENT

| Element | Average Anode Source of Both Cathodes | Average Wirebar from Tough Cathodes | Average Coalesced from Brittle Cathodes | OFHC Copper | |
|------------|---|---|---|--|---------------------|
| | | | | Anode | Wirebar |
| Cu..... | 99.4902 | 99.9534 | 99.9871 | Anode source analysis not known ^d | 99.9800 |
| O..... | 0.1544 | 0.0372 | 0.0035 ^a | | 0.0000 ^b |
| S..... | 0.0050 | 0.0014 | 0.0008 ^c | | 0.0025 |
| As..... | 0.0015 | 0.0008 | 0.0007 ^c | | 0.0008 |
| Sb..... | 0.0022 | 0.0016 | 0.0013 ^c | | 0.0028 |
| Se + Te... | 0.0550 | 0.0002 | 0.0003 | | 0.0031 |
| Ni + CO... | 0.0780 | 0.0005 | 0.0005 | | 0.0016 |
| Fe..... | 0.0022 | 0.0005 | 0.0005 | | 0.0015 |
| Pb..... | 0.0440 | 0.0004 | 0.0005 | | 0.0004 |
| Ag..... | 0.1440 (42 oz.) | 0.0016 (0.47 oz.) | 0.0020 (0.58 oz.) | | 0.0016 (0.48 oz.) |
| Au..... | 0.0038 (1.1 oz.) | 0.000026 (0.0075) | 0.000033 (0.0097) | | |
| Else..... | 0.0197 | 0.002374 | 0.002767 | | 0.0057 |
| | 100.0000 | 100.000000 | 100.000000 | | 100.0000 |

^a No oxygen is detectable by microscope in coalesced copper. The 0.0035 shown is by ignition in hydrogen and it is the opinion of the writer that it arises mainly from surface oxidation in the sample drillings, plus possible absorbed and/or adsorbed oxygen.
^b The oxygen shown is stated to be by microscope.
^c Sulphur, arsenic and antimony are partially removed during the gas cleaning.
^d The analysis of the anodes from which OFHC copper is produced is, unfortunately, not known to the writer.

hence there tends to be slightly more entrapment of some of these electrolyte-insoluble substances on the brittle-cathode face than on the corresponding smoother tough-cathode face, other operating conditions being the same in each case.

SURFACE CHARACTERISTICS

The main difference between coalesced copper and all other brands is: (1) it is not melted; (2) it is not cast; (3) it is not hot-rolled. These three unique differences ensure a remarkable smooth surface, substantially free from the imperfections that often pierce the insulation surrounding the windings of motors, transformers, etc., and thereby constitute one of the principal causes of short circuits in electrical equipment. Surface perfection is a relative term, therefore the statements made here regarding this property of coalesced copper must be accepted in that sense. However, the general superiority of coalesced copper in this regard has been quite well established. It has been termed "sliverless copper."

When these curves are superimposed or are compared with those of Webster, Christie and Pratt, only such slight variations and differences occur as are normally to be expected in determining characteristics of this nature. No trend (except as noted below) is discernible from any of the data at hand. Coalesced copper, being oxygen-free, has the characteristic virtues and properties of this class of metal. Needless to say, it is definitely superior to hot-rolled tough-pitch copper in ductility. Coalesced copper and OFHC are equivalent metals as to ductility when measured by the usual laboratory twists and contraction of area tests. Ordinary commercial specification values for copper are representative of the range of tensile strength, elongation and grain size of coalesced copper; and it readily meets the now generally used hydrogen-anneal-bend test for oxygen-free copper.

COLD-WORKING AND ANNEALING

Owing to its perfection of surface and freedom from oxide, coalesced copper has

the capacity for almost unlimited cold-work without any annealing. As an example, the writer has seen a $2\frac{1}{2}$ -in. round bar cold-rolled without anneal to a 0.040-in. thick strip and a $\frac{7}{8}$ -in. rod cold-rolled to a 0.010-in. thick strip without annealing. In neither case did edge cracking occur.

Many of the impurities present in copper alloy with it. In coalesced copper, however, they do not alloy uniformly throughout the entire body of the metal, as when copper is melted and cast. In coalesced copper, each of the individual impurity particles alloys (if at all) only locally over limited microscopic or submicroscopic areas and hence affect the physical properties relatively little. As the late W. H. Bassett, of the American Brass Co., pointed out many years ago, silver alloyed with copper raises the annealing temperature and, conversely the absence of silver lowers the annealing temperature. Since the silver present in coalesced copper remains substantially unalloyed with the body of the metal, the temperature-time required for annealing is markedly lower than all other coppers. This very low temperature-time annealability, the almost indefinite cold-working capacity (alluded to above) and the electrical conductivity (shown below), constitute three factors of very considerable importance, both technically and commercially.

ELECTRICAL CONDUCTIVITY

Table 2 shows the electrical conductivity of coalesced copper in comparison with those of other copper. The figures on coalesced copper represent the average of many determinations over a period of several years.

ACKNOWLEDGMENTS

Opportunity is taken to express appreciation to Phelps Dodge Corporation for the courage to embark on the development of so revolutionary a process and to Messrs.

Wylie Brown and Horace Staples, of the Phelps Dodge Copper Products Co., for their steadfast confidence in and support of the development program; to the Executive Committee of the American Smelting and Refining Co. for permission to conduct the development at their multiple-system Perth Amboy refinery, when it became apparent that the series system at Laurel Hill was

TABLE 2.—*Electrical Conductivity of Coalesced Copper and Other Coppers*
PER CENT I.A.C.S., at 0.081-INCH DIAMETER
ANNEALED WIRE

| Copper | Maximum | Minimum | Average |
|--|---------|---------|---------|
| Coalesced copper extruded and cold-worked..... | 102.3 | 101.5 | 101.80 |
| Coalesced copper extruded, hot-rolled and drawn..... | 101.7 | 101.4 | 101.53 |
| Electrolytic copper from same anode source..... | 101.6 | 101.0 | 101.42 |
| Typical American electrolytic wirebar..... | 101.2 | 101.1 | 101.15 |
| OFHC: samples taken from bars, May 1936..... | 101.0 | 100.7 | 100.82 |
| Published by U. S. Metals Co., Jan. 1932. | | | 100.63 |

not readily adaptable to the production of brittle cathodes of the required characteristics; to the Revere Brass and Copper Co. for throwing open all the operating and cost data of its extrusion plant; to W. H. Peirce and the organization at the Perth Amboy refinery for their intense interest and wholehearted help during the protracted commercial development at Perth Amboy; to the designing engineers of both the Watson-Stillman and W. S. Rockwell companies for the extraordinary interest and help in overcoming new mechanical obstacles as they were encountered during the research and design; to the writer's associate, John Tyssowski, for his very effective supervision of the administration, financing and legal work of the patent-holding company; and last, but not least, to W. H. Osborn and his assistant, H. H. Stout, Jr. The two men last named took the brunt of the continuous daily struggle to overcome any and all obstacles, necessarily encountered in such a

revolutionary development, and although at times they met many difficulties neither of them ever wavered, insofar as the writer could observe.

As a corollary, the writer cannot resist expressing his admiration of the American Metal Co. and the Scovill Manufacturing Co. for having had the courage and the vision to take the initiative in expending the large amount of money necessary to do the pioneer work that made oxygen-free, high-conductivity copper a commercial reality. They deserve the gratitude of all copper fabricators.

DISCUSSION

(W. H. Bassett, Jr., *presiding*)

C. S. SMITH,* Waterbury, Conn.—The author comments on the fact that coalesced copper has a lower recrystallization temperature than copper produced by the conventional processes. This is probably because the inevitable traces of silver and other impurities are not uniformly distributed in solid solution. Any heat-treatment or process anneals subsequent to the extrusion, therefore, will tend to cause solution of those impurities and hence will raise the temperature of recrystallization. Can the author give specific data on this effect?

E. E. SCHUMACHER,† New York, N. Y.—Mr. Stout deserves many thanks for presenting an interesting and instructive paper. Additional information pertaining to the drawing characteristics of coalesced copper rod to 36-gauge wire, or smaller, would be welcome.

H. H. STOUT (author's reply).—The very few processing anneals required in the commercial cold-working of coalesced copper have not dispersed the silver or other impurities to a point where it has caused any increase in the unusually low time-temperature requirement of any subsequent process anneals. However, no investigation has been made as to whether or not a heat-treatment either excessively prolonged or carried on at an excessively high temperature would alter this characteristic of coalesced copper.

Coalesced copper can be drawn into fine wire. In drawing down to about 0.010-in. diameter, its performance is approximately the same as that of any other good grade of copper. Below this size, however, more breaks are usually experienced than with other coppers. This feature can be, and has been, overcome by tightening the technique of some process controls in the tankroom and slightly altering such controls in the smelter casting of anodes. The cylindrical, basic, brick-lined smelter anode furnace does not, per se, produce the sticky acid slag formed in the standard refinery silica-brick reverberatory, which acts as a collector for the occluded basic slag and magnetite carried forward in the blister from the converter and which, via the anode, may become entrained on the cathode face. To perform this function, a suitable synthetic slag would have to be introduced as well as the installation of a slag bar in the smelter anode-pouring ladle. The author is advised that to date it has not been found profitable to incur this increased cost, covering (as it would) the entire output for the sole purpose of supplying the relatively small amounts that would be used for drawing wire below 0.010-in. dia. The most advantageous field for coalesced copper is currently in the coarser sizes of wire and in rods and flats.

* Research Metallurgist, American Brass Co.

† Research Metallurgist, Bell Telephone Laboratories.

The Coalescence Process for Producing Semifabricated Oxygen-free Copper

By JOHN TYSSOWSKI,* MEMBER A.I.M.E.

(New York Meeting, February 1941)

IN 1925, Harry Howard Stout, then metallurgist for Phelps Dodge Corporation, while investigating the cleaning of cathode copper by various gases at elevated temperatures below the melting point of the metal, observed in the laboratory that particles of pure copper heated in a closed tube filled with hydrogen seemingly "stuck together."

By further investigation he found that there was actual crystal growth across the boundaries of the particles of pure metal; in other words, there was a complete new crystal realignment and growth throughout the newly formed copper mass. It was *coalescence*, not *adhesion*; the several particles had become one unit. From this discovery has been developed the coalescence process, whereby copper of cathode purity is squirted out in semifabricated form from an extrusion press, by the application of about 3000 tons pressure on a 10-in. piston.

Stout decided that cathode copper produced by electrolytic deposition was the logical source of the pure copper required for the coalescence process, but as there was no way of reducing the ordinary tough commercial cathodes to the small particles required he was confronted by a serious problem at the outset. Under his direction, this problem was solved by William H. Osborn and Harry Howard Stout, Jr. They developed the process and technique for producing cathode copper in brittle, friable

form, and to them must be given the greater part of the credit for this phase of the development program as well as for that relating to the gas cleaning of the cathode particles.

Concurrently, the three metallurgists worked on the problem of effecting a complete union of the cathode particles. Adequate washing was all that was needed to free the particles from electrolyte solution and slimes. A press was designed to produce briquettes of the proper porosity and density, and a method was devised of removing surface oxidation from the particles of cathode, by treatment in an atmosphere of deoxidizing gas at an elevated temperature. The temperature was determined at which the surface cleansing and preheating could be done in one operation, and for this a charging and preheating furnace in which there is maintained a positive pressure of deoxidizing gas atmosphere was designed. And finally, a method of feeding the heated briquettes of deoxidized cathode copper into an extrusion press without contamination from the air was evolved. For the final stage, a press was required because not only heat but pressure was required to obtain complete growth of the new crystals between the cathode particles as well as the elimination of all voids or non-coalesced areas.

All essential stages of the process are protected by patents or patent applications in the United States and principal foreign countries, and the copper is produced on a commercial scale.

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* President, Copper Deoxidation Corporation, New York, N. Y.

STEPS IN PROCESS

The successive steps of the coalescence process are:

1. Production of a suitable anode.
2. Production of cathode copper in brittle, friable condition, easily broken into small particles.
3. Washing of the particles.
4. Pressing the particles into briquette form for convenient handling.
5. Removal of oxygen (oxides, sulphates, sulphur, etc.) from the cathode particles constituting the briquette by washing with a suitable deoxidizing gas mixture, at the same time heating the briquette mass to the proper temperature for the last step.
6. Coalescing the copper particles by pressure into solid form entirely free from voids and extruding the metal in semifabricated shapes.

PRODUCTION OF ANODES

The process starts with the production of a suitable anode, which involves standard practice except as to the elimination of impurities introduced from the mold wash. This has been accomplished by using a mold wash with a melting point higher than the melting point of copper, which protects the mold but goes into solution in the electrolyte during the production of brittle cathodes. Zinc oxide meets these requirements. Silica and silicates are the principal deleterious materials to be eliminated.

PRODUCTION OF BRITTLE CATHODES

Product

The essential requirement is to produce an electrolytic copper cathode that can be easily stripped from the re-usable blanks and is friable, so that it can be easily broken into small fragments.

Theory of Brittle Cathodes

The deposition of brittle cathodes involves the formation of relatively scattered original crystal nuclei and the impeding of

coherence of these to each other as they build up; at the same time the impeding of the adherence of these nuclei and accretions to the blank upon which they are deposited.

This result is obtained by two means: (1) The formation of a film of definite insulating or dielectric strength on the blank, which causes the current to puncture, and hence copper to deposit, at relatively separate points; (2) the subsequent wetting or filming of these scattered crystal nuclei to prevent their interlocking or cohering into a tough or nonbrittle mass. This effect is produced by the use of a substance that has the power to preferentially wet copper in respect to the electrolyte.

Practice of Making Brittle Cathodes

The making of brittle cathodes differs from standard American refinery practice for electrolytic deposition of refined copper in the following points:

1. Glue is omitted from the electrolyte and an embrittling agent is used. A mixture of corn oil, castor oil, gasoline and carbon tetrachloride has been found satisfactory, forming an oil containing unsaturated hydrocarbons with dielectric strength in the film, which adheres to the blank. This ensures the formation of sufficiently separated starting crystals on the blank and also the prevention of the adherence and interlocking of these separated crystals (as they grow) to form a tough or nonbrittle cathode.

2. Depositing blanks (instead of starting sheets) are made of $\frac{1}{8}$ -in. cold-rolled polished copper sheets, so constructed as to avoid buckling. The surface is cleansed of oxide before use. Blanks may require amalgamation of surface before first use. Blanks are dipped in embrittling agent, removed, and allowed to drain for a short time in air before being placed in depositing tanks.

3. The cathode is shaken or knocked off and broken to the desired size and the depositing blanks are again used by repeating the cycle.

In making brittle cathodes, standard American refinery practice is employed as follows: (1) multiple system preferable; (2) depositing tanks, construction and dimensions; (3) salt used to control chlorine; (4) rate of circulation of electrolyte; (5) temperature of electrolyte; (6) acid content of electrolyte; (7) length of deposit cycle; (8) dimensions of anodes, weight and spacing in tanks; (9) thorough washing of cathode deposit.

Data regarding production of brittle cathodes on a commercial scale, over a period of several years, indicate a power consumption of only 75 to 85 per cent of that for standard tough cathodes under similar operating conditions—multiple system, Baltimore groove contacts, current density, solution temperature, circulation, acid content, etc. This is evidenced in the smaller amount of power required per ton deposited, or greater poundage deposited per kilowatt-hour. The explanation is in the lower resistance on account of the omission of glue from the electrolyte and the solid instead of loop contact on the cathode starting sheets. A further economic factor in favor of the brittle operation accrues from the re-usable starting sheets. The major disadvantage is evidenced in a tendency toward somewhat higher labor costs occasioned by the application of the embrittling agent, removal of the cathode deposit, rehandling of the starting sheets and the importance of intelligent tank-house inspection. Also, silver and gold losses are indicated as likely to be somewhat greater in brittle-cathode operations probably because of the comparatively rougher nature of the deposit and consequent possibility of greater entrapment of slime. The losses obviously increase with the precious-metal content of the anodes and also with the roughness of the cathode face, hence proper control of the factors affecting the size of the deposited cathode crystals assumes considerable importance.

WASHING THE BRITTLE CATHODES

Washing the brittle cathodes is performed with the same degree of efficiency and with the same water pressure and temperature used for similar purpose in making tough cathodes.

BRIQUETTING

In this stage of the process the particles of brittle cathode are compressed, cold, into a briquette (bale) of 80 to 86 per cent density of solid copper. This requires a pressure of about 20,000 lb. per sq. in. on the baling press plunger. A briquette is produced in which the separate particles interlock one with another to form a porous mass, which maintains its form in subsequent handling. At the same time the briquetted mass is permeable to the cleansing fluid subsequently used. The briquettes are then passed through the heating furnace, which is also a cleaning furnace.

PURIFICATION AND DEOXIDATION

Purification and deoxidation are accomplished in a controlled-atmosphere heating furnace through which the briquettes are passed en route to the extrusion press. In this furnace the briquettes are brought up to a temperature of 1600° to 1670°F. in a deoxidizing atmosphere. Partially burnt illuminating gas or propane gas (C_3H_8), nitrogen, steam or hydrogen are suitable agents when properly controlled and proportioned. The furnace atmosphere must be kept at a continuous positive pressure sufficient to prevent any suck-in of air when the furnace doors open for the introduction of the briquettes. These are sufficiently porous to permit the penetration of the gas, which, at the temperature, removes any traces of oxygen and effects a substantial reduction of the arsenic and antimony content from the brittle-cathode crystal particles. Sulphur is reduced to a fairly constant figure of about 0.0008 per cent. Hence, at this stage of the process.

the cathode copper is brought to a higher purity than when originally electrolytically deposited. It then passes direct to the extrusion press through a controlled-atmosphere chamber, thus preventing reoxidation.

COALESCENCE AND EXTRUSION

Coalescence and extrusion are accomplished in a press that exerts a pressure up to about 76,400 lb. per sq. in. on the plunger. Actual pressures during extrusion vary from 30,000 to 53,000 lb. per sq. in. for normal sizes up to the press maximum for small cross-section areas. The discovery on which this process is based relates to the complete crystal growth between all parts of all the copper particles under pressure at a temperature below the melting point when the surfaces are properly cleaned. A complete new grain structure develops between the copper particles when all surface impurities are eliminated; and the extruded product is of the highest purity and of uniform physical character. The size and cross section of the extruded product are limited only by the dies used and certain economic considerations. In practice, it has been found uneconomical to extrude an article of much below 0.5 sq. in. cross-sectional area or much above 4.5-in. diameter. Rounds, rectangles and special shapes are regularly extruded.

The hydraulic system to operate the coalescence press is the same as that used by standard copper or brass extrusion presses to handle products of similar sizes.

CHARACTERISTICS OF COALESCED COPPER

Comparative Chemical Characteristics

Coalesced copper is an oxygen-free copper. As far as other impurities are concerned, coalesced copper as compared with any fire-refined copper made from the same blister source will contain considerably less arsenic and antimony, owing to the relatively large amount removed by the gas cleaning of the briquetted brittle cathodes, and for the same reason the sulphur content

is substantially lower than that of any commercial brand of fire-refined copper now on the market. Other impurities, such as nickel, cobalt, selenium, tellurium, or iron, are virtually the same as in any high-grade tough-pitch or oxygen-free copper produced from tough cathodes electrolytically deposited from anodes of the same composition as those from which the coalesced brittle cathodes are made.

Physical Characteristics

Shapes.—The pure copper can be coalesced and directly extruded in any of the usual shapes (such as angles, tees, bars, rods, tubing) that have a cross-sectional area greater than 0.5 sq. in. This eliminates the usual fabrication required to produce these shapes and sizes from any cast product. A bar with a maximum cross-sectional area of 20 sq. in. can be extruded from a press handling a briquette 10 in. in diameter.

Surface.—The surface of the product as extruded or after subsequent cold-working is superior to hot-rolled copper now on the market. It has been called "sliverless" copper. The smooth surface is one of the characteristics in which it is markedly superior to other coppers, and makes it particularly suitable for use in the electrical trade, where a single surface sliver may ultimately cause a puncture in the insulating material and necessitate the rewinding of a motor generator or transformer.

Electrical Conductivity.—Electrical conductivity averages about 0.3 per cent I.A.C.S. higher than electrolytic tough-pitch copper produced from the same blister copper source.

Number of twists; 90° bends; percentage of elongation and percentage of contraction of area are substantially the same as those of the best brands of oxygen-free or deoxidized copper now on the market, and well above ordinary tough-pitch electrolytic.

Ductility.—Coalesced copper has the capacity for almost unlimited cold-working

without the necessity of ad interim anneals. This feature, together with the fact that products of 0.5 sq. in. cross-sectional area can be directly and economically extruded, means that no hot-rolling of coalesced copper is required in order to furnish the commercial shapes now ordinarily in use, such as rod, bull rings, flats, bars, tees, angles.

Tensile Strength.—The tensile strength, both hard-drawn and annealed, is of the

same order of magnitude as other coppers for the same degree of processing.

Annealing.—The grain sizes found in annealed coalesced copper tend to be slightly larger than those found in other copper with the same temperature and time of anneal. Furthermore, the annealing-temperature range of coalesced copper is well below other coppers, thus making possible definite savings of time and expense in annealing operations.

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